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# FUNDAMENTALS AND APPLICATIONS OF THE ICP

by

JENNIE LILLIAN SETO

(C)

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

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Dedication

To my father and mother

## ABSTRACT

The inductively coupled plasma is rapidly gaining in popularity as an excitation source for atomic spectroscopy. The study undertaken here delved into both fundamental characterizations and applications with the plasma.

In the first half of this thesis atomic absorption spectrometry was investigated as a means for obtaining greater insight into plasma characteristics, including population densities and temperature. The setup used two plasma excitation boxes - one acting as a source of radiation and the other as an atom reservoir. It was shown that absorption in the plasma is indeed possible for analyte species. The author only briefly examined this method of characterizing the plasma before going on to investigate applications with the plasma.

The second half of the thesis used a commercial system with direct reading capability to determine the elemental compositions in real samples rather than simply studying laboratory prepared solutions, as was the case in Part I. Results for standards received from the National Bureau of Standards gave good agreement with certified values.

It has been shown that ICP analysis can be used to provide answers in numerous analytical applications. This is steadily being substantiated by the increase in plasma publications and commercial systems becoming available to the user.

ACKNOWLEDGEMENTS

I would like to thank everyone in the Chemistry Department, past and present staff, who have helped me to broaden my knowledge and to attain my goals. This list is endless, but special thanks go to my research advisor, Gary Horlick; fellow colleagues, especially Will Pettit; and the professors in the Analytical Division.

Gratitude and love are also extended to Norbert Wolter for without his assistance, persistance and endurance through the final phases, this thesis would not have been completed.

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# Part I

## Inductively Coupled Plasma - Atomic Absorption Spectrometry

# CHAPTER I

## ATOMIC ABSORPTION MEASUREMENTS WITH THE ICP

> The introduction of the inductively coupled plasma (ICP) spectroscopic source came at a time of exponential activity in atomic absorption spectrometry (AAS) and the capabilities of the ICP for single element analysis had to match those of AAS. Not until 1969 could this claim be made for the ICP. The interest in AAS channeled some of the early ICP studies toward testing the ICP discharge as an atom reservoir for AAS.

Barnes (1) made this statement in a review discussing the advances in the area of ICP's. He goes on to say that exploratory measurements with ICP-AAS were made by numerous authors in the late 60's. They included Wendt and Fassel (2), Greenfield et al. (3), Barnett et al. (4,5) and Veillon and Margoshes (6). In 1976 Abdallah et al. (7), in a French article, suggested reasons for the limited capabilities in the early measurements made via ICP-AAS.

As this mode of analysis did not take hold, researchers went on and started to investigate the usefulness of the ICP in an emission mode. Since the late 60's and early 70's the ICP has come to be extensively studied via atomic emission spectrometry (AES). This can be seen by the numerous papers published yearly on the ICP as well as the advent of new journals totally devoted to the inductively coupled plasma. An example of such a plasma journal which is widely accepted in the literature is ICP Information Newsletter edited by Barnes.

Much work has been done with ICP-AES to characterize

plasmas. Information has been obtained and is still being tabulated and expanded in the areas of population densities, temperatures and mechanisms (8-24).

Recently a paper has been published suggesting another means of obtaining the desired information in a less tedious manner. 'Why not ICP as atom reservoir for AAS?' is the title of this paper by Magyar and Aeschbach (24). Here they discussed the sensitivity of determination by ICP-AAS over flame-AAS. They stated:

> Like flame-AAS, an analytical approach using ICP-AAS has high selectivity and makes it possible to carry out determinations without chemical and ionization interferences.

In their work Magyar and Aeschbach found that temperature and number density of free electrons depend on the position in the plasma and that the number density of the absorbing atoms varies along the absorption path length. Sensitivity was influenced by the divergence of the light beam from their source, a hollow cathode lamp (HCL), and by the height above the load coil of the torch in the ICP excitation stand.

Another group using ICP-AAS operates in Japan under the direction of Fuwa (21,22,23). In their work Uchida et al. proposed the use of a microwave induced plasma (MIP) as the source for their measurements of number densities of metastable argon atoms and electrons, of spatial distributions of metastable argon atoms and of argon excitation temperature. They determined the argon excitation temperature and electron number density near the center of the plasma to be 7000K

and $5 \times 10^{15}$ $cm^{-3}$.

In this work an ICP is proposed as the source for ICP-AAS, in other words, a dual plasma system. The reason for this choice will be elaborated in the next chapter.

## CHAPTER II

## SOURCES FOR ICP-AAS

### A. Introduction

A major requirement for ICP-AAS is the availability of an intense line source. Several authors have used hollow cathode lamps (HCL) as sources (6,9,24). Other light sources used include argon sealed electrodeless discharge lamps (EDL) of mercury (22), xenon arc lamp as a continuum source (22), and an atmospheric pressure argon microwave induced plasma (MIP) (21,22,23). However, drawbacks exist with each of these sources.

To facilitate measurements in absorption, spectral lines must meet the following criteria. The spectral lines emitted by the source should be sufficiently intense to enable discrimination against the lines emitted by the plasma, that is, the background intensity emitted when the solvent is introduced into the plasma. For the ICP thermal radiance, including 'Bremsstrahlung', is much more intense than in a flame where analysis using the atomic absorption mode is feasible due to the lower temperature existing in the flame (6,9,24).

### B. Hollow Cathode Lamps

Some elements cannot be satisfactorily determined by absorption in a plasma because with the HCL as source, its source emission is considerably weaker than the emission of

that element in the plasma tail flame. A lock-in amplification system can process the modulated source signal of the HCL from the unmodulated sample emission or the dc signal level in the plasma and discard the noise associated with the element emission signal. However, with high plasma intensities the dc signal from the plasma often produces a high noise level in the signal. If the intensity from the HCL exceeds or equals the intensity from the plasma, then absorption measurements are generally possible.

In order to obtain as low as possible relative background intensities the HCL must be operated at maximum lamp currents suggested by the manufacturer or through the use of a pulsed HCL, with current capabilities extending from 50 to 500mA, coupled to a boxcar integrator (9).

The HCL is used extensively in flame-AAS. It is less suitable for ICP-AAS because the ICP exhibits high temperatures and high number density of free electrons. These two factors give rise to a higher population of ions rather than ground state atoms in the plasma. The HCL is really only suitable for the investigation of neutral atoms such as Ca I (422.7 nm) or Mg I (285.2 nm). As the flame is lower in temperature, approximately 1500K, compared to about 5000K in the plasma (25), fewer atoms are excited and the ion population in flames is low. Thus absorption measurements with a HCL and a flame are possible. To enable measurements using HCL-ICP-AAS higher lamp currents and/or lower plasma powers would be necessary.

In the work conducted by Magyar and Aeschbach (24) they state that with the HCL as the source for ICP-AAS, atomic absorption should occur above 1.6 kW RF power, but was not measurable because the atomic emission from the plasma was too intense. Therefore it was noted that the utility of the discharge in atomic absorption depends on the intensity of the emission from the HCL source relative to the emission intensity of the analyte lines emitted by the plasma.

Veillon and Margoshes (6) state that the detection limits for the elements they studied via absorption were relatively poor, but they expect that more intense line sources will improve the detection limits by increasing signal-to-noise ratios.

C. Electrodeless Discharge Lamps and Xenon Arc Lamps

Uchida et al. (22) found that as light sources the argon sealed EDL of mercury and the xenon arc lamp were not successful. The EDL was unsuccessful because the radiation appeared to be too weak to overcome the intense emission of the ICP, similar to the problem found by researchers using HCL's as a source. Xenon arc lamps were not successful either in their work because the sensitivity of atomic absorption using a continuum source was too low when coupled to a low resolution monochromator.

D. Microwave Induced Plasmas

In other work done by Uchida et al. (21,22,23) the MIP was found to be successful in the application of atomic absorption measurements on metastable argon (811.5 nm) density. The reasons given were the sharp spectral profile and the stable and high emission intensity provided by the MIP.

Various important conclusions were cited in Uchida's work. He found absorbance increased about two times with the increase of RF power from 1 to 2 kW. This, he indicated, meant the number density of metastable argon atoms increased with power. He also found the number density of the argon metastables decreased with an increase in carrier gas flow rate. They reasoned that this was due to the cooling effect of the cold carrier argon and the water mist in the discharge. Absorbance or number density of metastable argon atoms remained constant even with the introduction of increasing amounts of potassium, an easily ionizable element, into the plasma.

E. Inductively Coupled Plasmas

All of the sources mentioned so far for ICP-AAS analysis have been less than satisfactory. This is due to the fact that the ICP itself is such an intense light source in comparison to any of these other sources. In this study the ICP is proposed as the light source for ICP-AAS, in other words, a dual plasma setup where one plasma acts as

the source for atomic absorption measurements and the other as the atom reservoir. The ICP is also useful as a source because of its multielement capabilities which are limited in each of the sources already mentioned. As well, both neutral atoms (I lines) and ions (II lines) for a number of elements can be studied. With flame-AAS, studies are limited to neutral atoms only. This is due to the lower thermal energy in a flame.

With the ICP, multielement analysis via atomic absorption is possible as similar multielement solutions can be aspirated into both plasmas. HCL's are restricted to the elements sealed in the tube and thus changes in elemental studies are more difficult as the lamp must be exchanged for one with the desired elements for study.

# CHAPTER III

## INSTRUMENTATION

### A. The Optical Setup

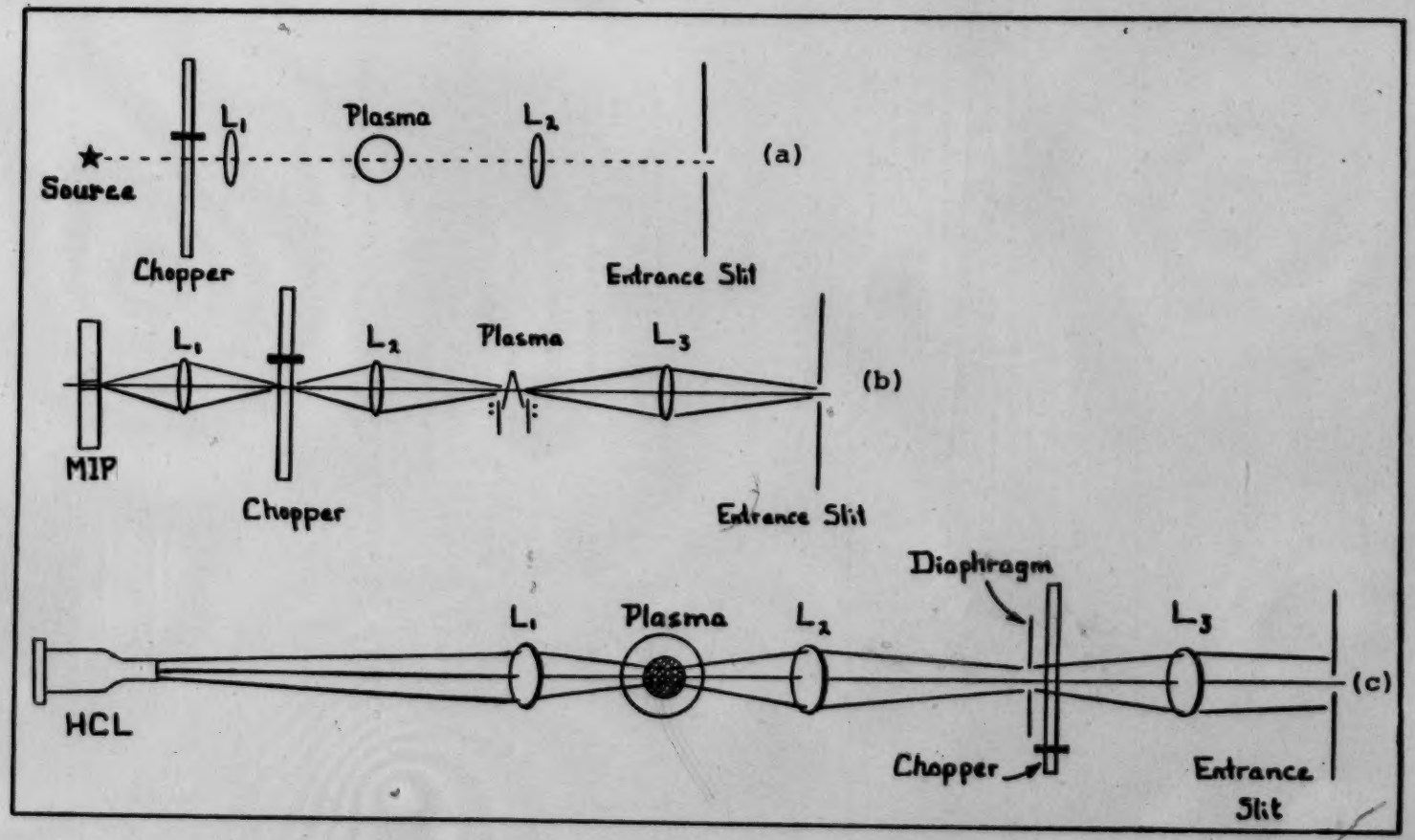
The optical setups used by authors employing atomic absorption as the mode of analysis with the ICP are illustrated in Figure 1. It was from this preliminary work by these other authors that the optical setup used in this work was devised.

Each optical setup shown in Figure 1 uses multiple lenses centered about the plasma which acts as the atom reservoir. The setup employed in the work by Veillon and Margoshes (6) is shown in Figure 1(a). The source they used in all cases was a variety of HCL's. The chopper was operated at a modulation frequency of 390 Hz. The fused silica lenses used in their work both had a focal length of 76 mm, but the type of imaging used was not mentioned.

Uchida et al. (22) used the setup shown in Figure 1(b). The modulation frequency of the chopper was 560 Hz. The three lenses were used to focus the radiation from the MIP on the chopper, on the center of the ICP, and on the entrance slit of the monochromator. The diameters of their focussed beams at these positions were less than 1 mm.

The final setup shown in Figure 1(c) corresponds to that used in Kornblum and deGalan's work (8). Actual dimensions and operating conditions for their setup were not given.

Figure 1. Various Modes of Optical Arrangement for ICP-AAS. See text for details.




a) Setup used by Veillon and Margoshes (6).
b) Setup used by Uchida et al. (22).
c) Setup used by Kornblum and de Galan (8).

From this study of how other researchers developed their optical setups, two optical arrangements were used in this dual plasma fundamentals study. They are illustrated in Figure 2. The arrangement used initially is shown in Figure 2(a).

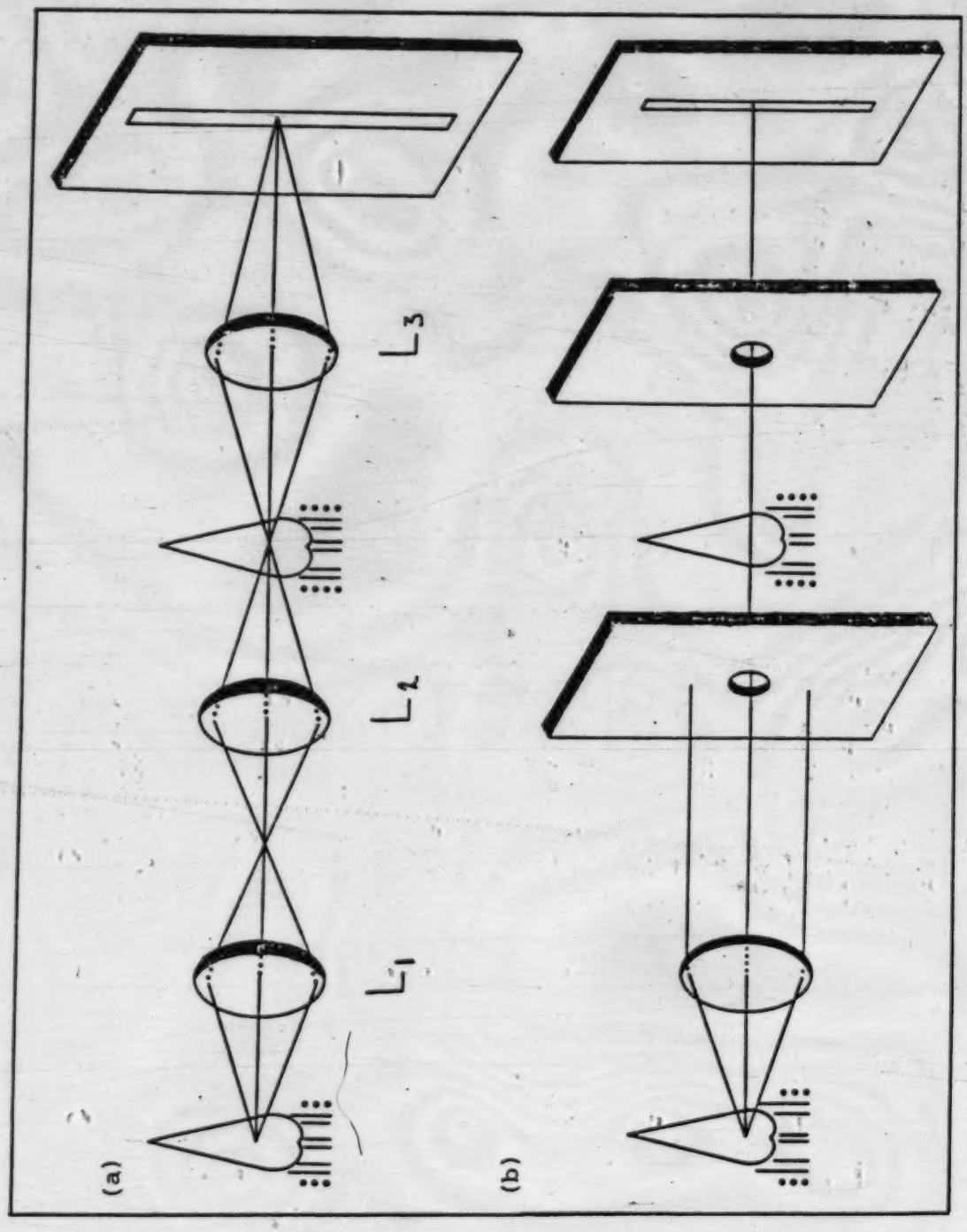
In this setup the source plasma, the first plasma, is recreated as a 1:1 erect image on the analyte plasma, the second plasma, using the first two lenses. $L_1$ and $L_2$ are 50 mm diameter Suprasil 1 lenses with focal lengths of 100 mm and 150 mm. Radiation is then focussed with $L_3$ (f=100 mm) onto the entrance slit of the monochromator. This setup was not found to be suitable for absorption analysis because the ICP emits intense radiation and with the setup shown in Figure 2(a), emission from both sources was compounded giving erroneous results. The emission from the analyte plasma could be eliminated via background subtraction when the radiation emanating from the source plasma was blocked. However, the emission from the source plasma could not be eliminated so easily with this optical arrangement.

The setup shown in Figure 2(b) minimizes the emission problems arising from the source plasma. With this arrangement the radiation from the source is collimated with a lens having a focal length of 300 mm. This collimated light beam passes through the radiation emitted by the analyte plasma and absorption is measured on a 1024 element photodiode array (PDA) coupled to a 0.3 m monochromator. The analyte

Figure 2. Optical Arrangement of Dual Plasmas for Fundamental Studies via AAS.

a) 1:1 erect imaging of source plasma using $L_1$ and $L_2$ followed by focussing with $L_3$ onto entrance slit of monochromator ($L_1$ and $L_3$, f=100mm Suprasil 1; $L_2$, f=150mm Suprasil 1).

b) Collimated light from source plasma using a single spherical lens (f=300mm Suprasil 1) is shone through analyte plasma onto entrance slit of monochromator. Apertures on either side of analyte plasma spatially select region of interest for atomic absorption measurements.


(a)
(b)
$L_3$
$L_2$
$L_1$

plasma was bracketted with apertures on either side to enable better spatial selection. These apertures also prevented saturation of the array from occurring prematurely when calibration curves were generated.

The latter optical arrangement was used in the studies carried out in this part of the analysis. The optical setup in Figure 2(b) is repeated in Figure 3(a). The actual layout of components on the optical railbed used is shown in Figure 3(b). The apertures were physically mounted on the analyte ICP matchbox as illustrated in Figure 3(b).

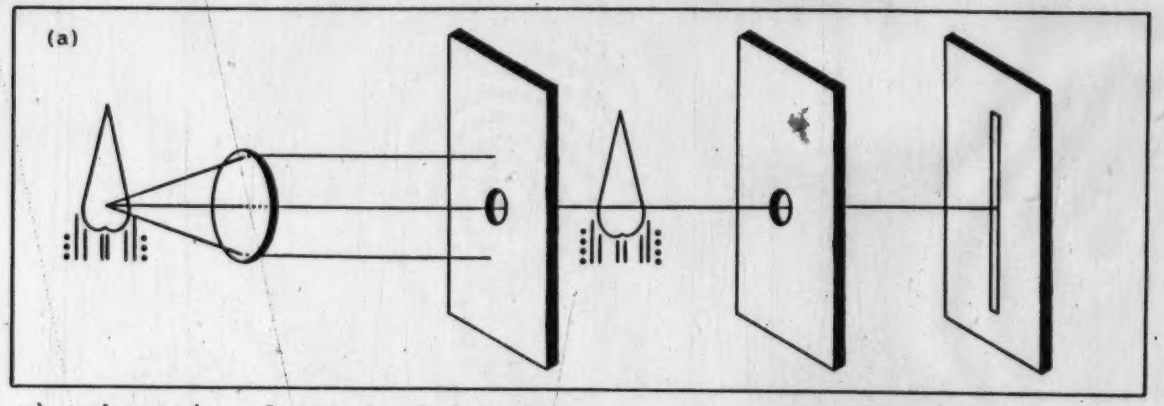
B. The Diode Array Detector

With the advantage of multielement capabilities in the plasma as previously mentioned, it would be foolish to choose a single channel detection system. In this study a self-scanning linear photodiode array (PDA) with a viewing window of 50 nm was used. The PDA was attached to a 0.3 m monochromator with Czerny-Turner mount. This detection system enables "absorption spectra" to be obtained.

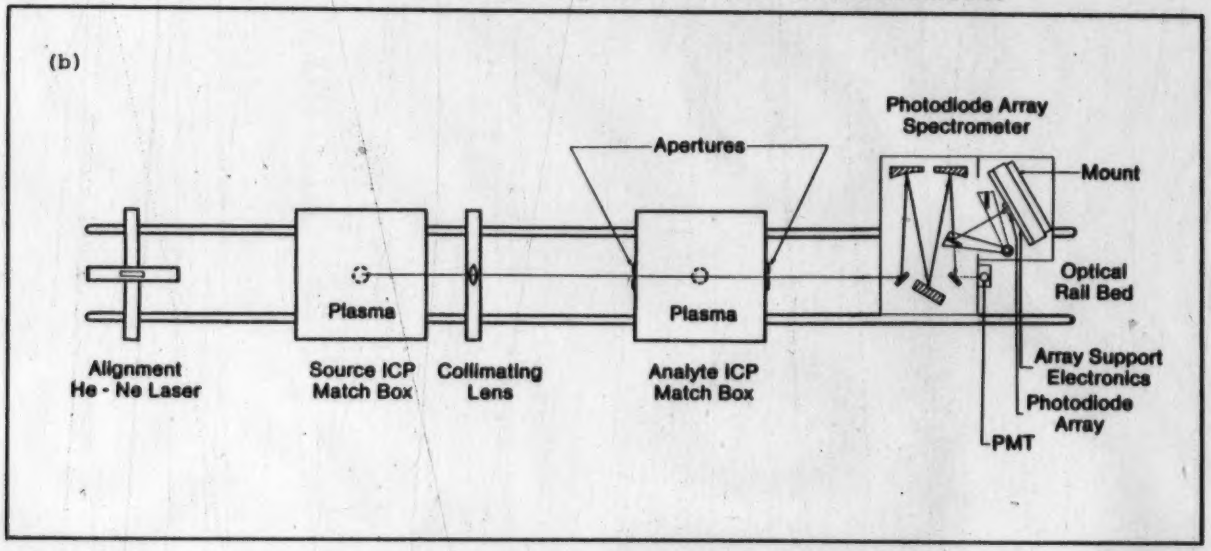
A larger diagram of the PDA spectrometer is given in Figure 4. The spectrometer is a GCA/McPherson 700 Monochromator with both photodiode array (PDA) and photomultiplier tube (PMT) capabilities.

The linear self-scanning silicon photodiode array used in the experiment was obtained from the Reticon Corporation, 910 Benica Ave., Sunnyvale, CA 94086. It consisted of 1024

Figure 3. Successful Optical Arrangement for ICP-AAS.




a) schematic of required imaging
b) actual rail bed mounting of plasmas and monochromator



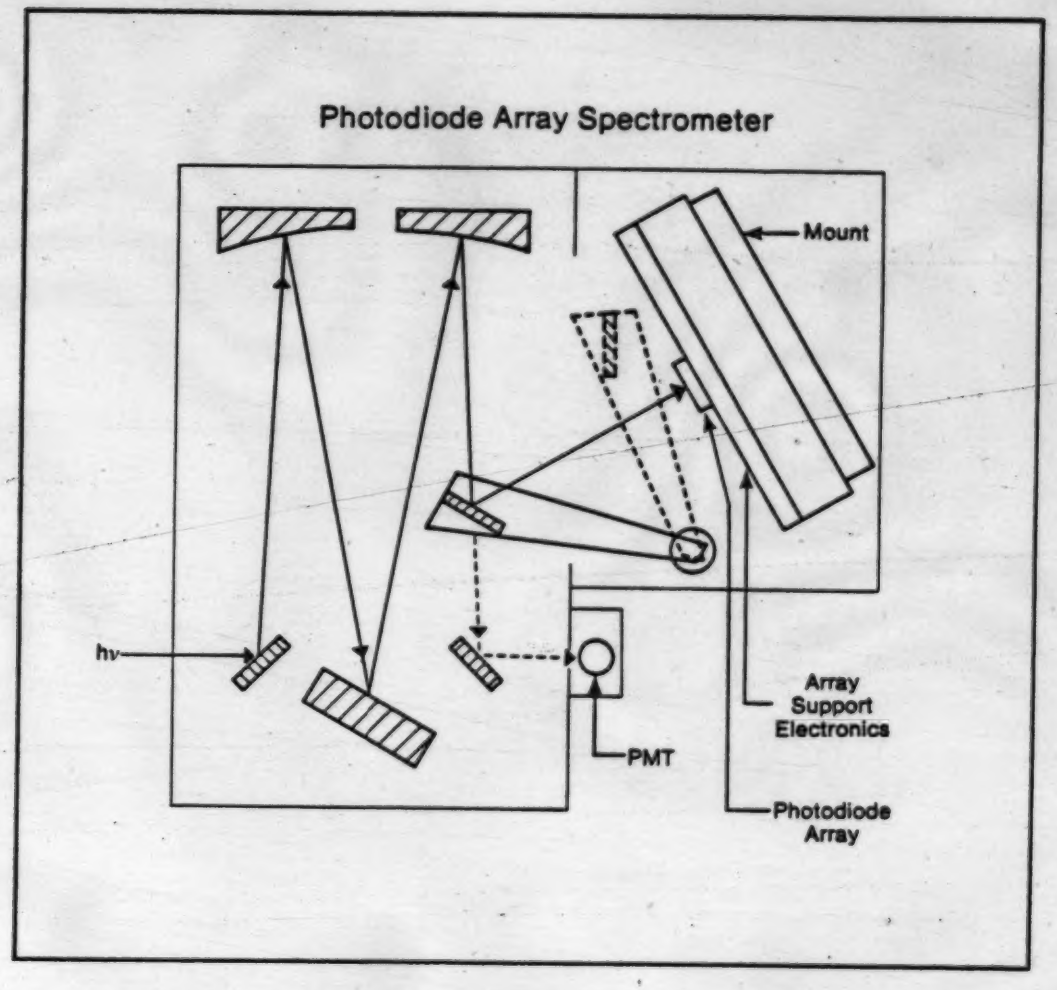



Figure 4. Schematic of Components within the Photodiode Array Spectrometer.

discrete diodes 0.43 mm (0.017") high on a 25.4 μm (0.001") spacing which results in a density of 39.4 diodes/mm and a length of 26.01 mm (1.024"). This 1024-element array facilitates the simultaneous measurement of neutral atom (I lines) and ion (II lines) absorption signals if both the I and II lines fall within this 50 nm window. An example of this is magnesium with a I line at 285.2 nm and two II lines at 280.3 nm and 279.6 nm.

C. Operating Conditions

Calcium and magnesium were chosen for this preliminary study as they are non-toxic elements. In the majority of this work the analytical concentration used in the source and analyte plasmas were respectively 5000 ppm and 500 ppm for the analyte species under consideration. Toxic elements, such as Cd and Zn, run at these concentrations without an adequate venting system would be extremely hazardous.

The source plasma is operated at a higher power than the analyte plasma. This coupled to the 10:1 ratio in concentration between source and analyte plasma allowed maximum absorption to be measured for the analyte species, calcium and magnesium.

A block diagram of the system used is given in Figure 5 and the operating conditions are listed in Table I.

D. The Torch

Two torch designs, illustrated in Figure 6, were used

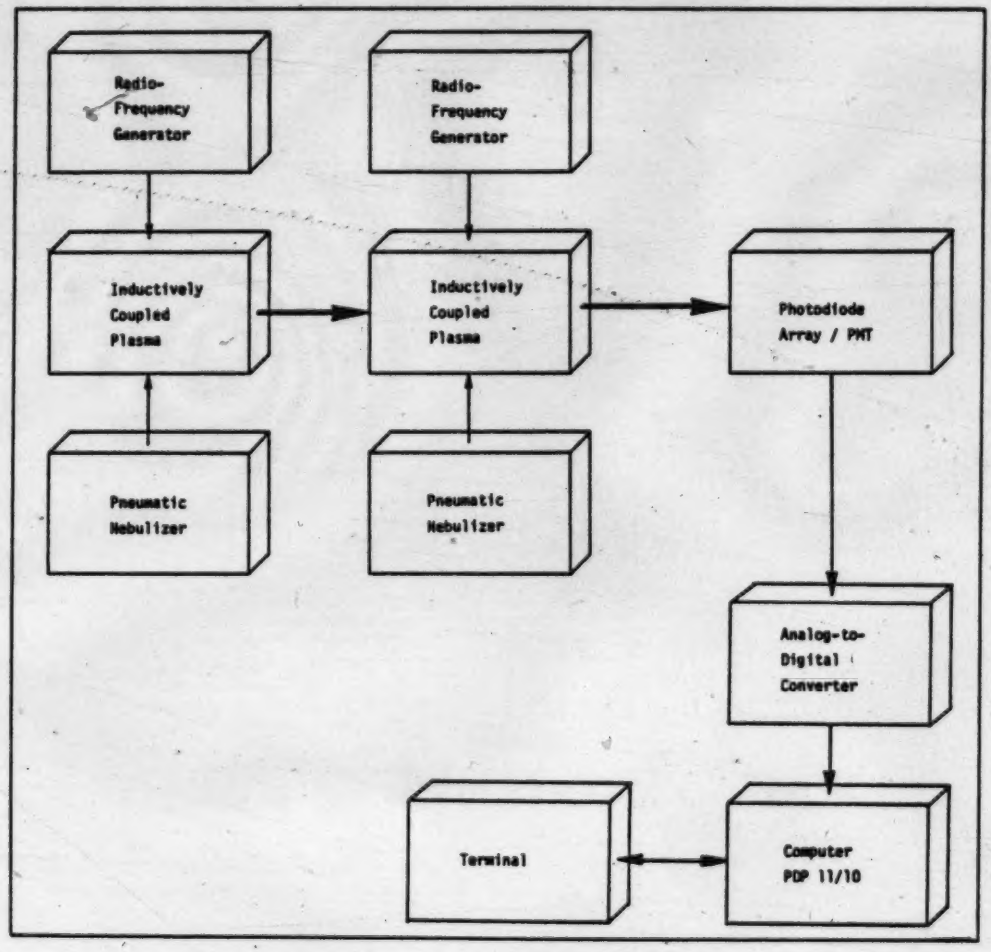



Figure 5. Block Diagram of Plasmas, Detection and Readout Systems.

Table I. Specifications for Typical Running Conditions.

| RUNNING CONDITIONS | | | |
|---|---|---|---|
| **Source Plasma** | | | |
| | Plasma-Therm ICP-2500 | Forward Power | 2.25 kW |
| | | Reflected Power | 0.0 kW |
| | | Frequency | 27.12 MHz |
| | | Coolant Gas | 20 l/min |
| | | Auxiliary Gas | 0 l/min |
| | | Nebulizer Gas | 0.5 l/min (20 psi) |
| | | Observation Height | 15 mm above l.c. |
| **Analyte Plasma** | | | |
| | Plasma-Therm ICP-5000 | Forward Power | 1.5 kW |
| | | Reflected Power | 0.0 kW |
| | | Frequency | 27.12 MHz |
| | | Coolant Gas | 20 l/min |
| | | Auxiliary Gas | 1.0 l/min |
| | | Nebulizer Gas | 0.5 l/min (20 psi) |
| | | Observation Height | 15 mm above l.c. |
| **Photodiode Array Spectrometer** | | | |
| | GCA/McPherson 700 Monochromator | Slit width | 100$\mu$m |
| | | Slit height | 12 mm |
| | Reticon Array RL 1024.S | Peltier Coolers | -15°C |
| | | Purge | $N_2$, 0.5 l/min |
| | | Clock | 15 kHz |
| **Analog-to-Digital Conversion** | | | |
| | Analog Devices ADC 1131J | Conversion Time | 12 $\mu$s |
| | | Resolution | 14 bits |

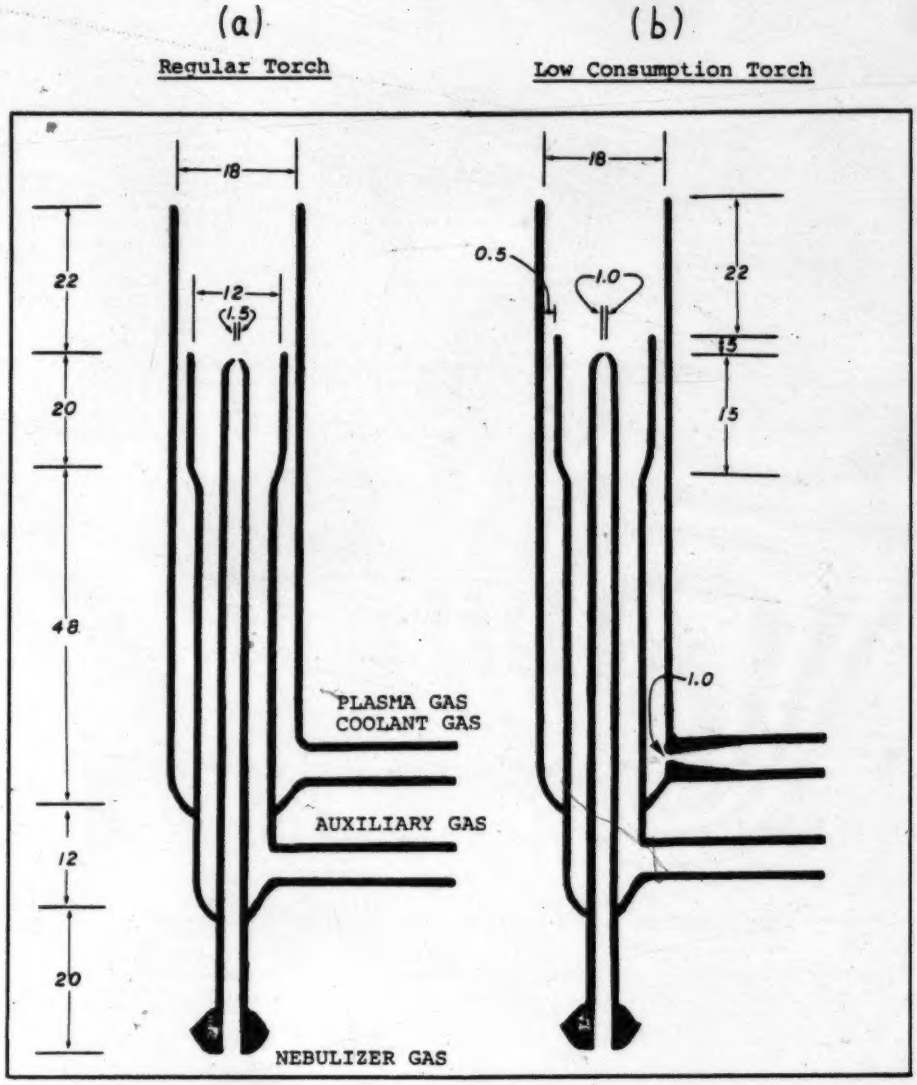



Figure 6. Dimensions for Regular Torch and Low Consumption Torch.

in the studies conducted here. The 'regular' torch design in Figure 6(a) is the design that has been most widely used both by our research group and others.

Argon gas consumption with the regular torch can be as high as 25 l $min^{-1}$ total argon. Though argon costs here in North America are not excessively high, the cost in Europe and other countries is often three times what it is here. Therefore extensive research has been carried out to find a method of reducing the argon consumption without sacrificing the desired properties of the plasma.

The most promising design to date is the 'low consumption' torch illustrated in Figure 6(b). The argon consumption is decreased by one-half or more due to the constriction placed in the coolant gas inlet and the smaller gap between the 'tulip' of the auxiliary tube and the coolant tube of the torch.

The plasma created in the low consumption torch can be operated at lower powers and has been found to be similar to a regular torch operated at higher powers, typically 2 kW (26).

Since the dual plasma setup is a heavy consumer of argon the low consumption torch was used in some of the work done here. No major discrepancies were observed between the two designs using the operating conditions outlined in Table II. No attempts were made to characterize these two torches in terms of their similarities and differences. The changeover towards using this newer torch was made simply

Table II. Comparison of Operating Conditions for the Regular and Low Consumption Torches.

| Regular Torch | |
|---|---|
| Source Plasma: | 2.25 kW power |
| | 20 lpm coolant gas |
| | no auxiliary gas |
| | 0.5 lpm-20 psi nebulizer gas |
| | 10000,5000,2500 ppm analyte species |
| Lens: | 30 cm focal length lens set at focal length for collimation purposes |
| 4mm aperture | |
| Analyte Plasma: | 1.5 kW power |
| | 25 lpm coolant gas |
| | 1.0 lpm auxiliary gas |
| | 0.5 lpm-20 psi nebulizer gas |
| | 500 ppm analyte species |
| 7mm aperture | |
| Detector: | Photodiode Array Spectrometer |
| | 100 micron slit width |
| | 25 or 100 seconds integration time |

| Low Consumption Torch | |
|---|---|
| Source plasma: | 1.5 kW power |
| | 12 lpm coolant gas |
| | no auxiliary gas |
| | 0.4 lpm-16 psi nebulizer gas |
| | 500 ppm analyte species |
| Lens: | 30 cm focal length lens set at focal length for collimation purposes |
| 4mm aperture | |
| Analyte plasma: | 1.0 kW power |
| | 10 lpm coolant gas |
| | 1.0 lpm auxiliary gas |
| | 0.3 lpm-10 psi nebulizer gas |
| | 1.25 mmolar analyte species with EIE and without EIE |
| 7mm aperture | |
| Detector: | Photodiode Array Spectrometer |
| | 100 micron slit width |
| | 25 seconds integration time |

to facilitate the use of less argon.

## CHAPTER IV

### ABSORBANCE MEASUREMENTS

Absorbance is defined by the expression $Abs=\log_{10}(I_O/I_T)$ where $I_O$ is the radiation transmitted through a blank, for example, water and $I_T$ is the radiation transmitted through the analyte. Figure 7 can be followed during the explanation. Magnesium will be used in the illustration.

Magnesium is aspirated into the source plasma at a typical concentration of 5000 ppm. For $I_O$ measurements water is aspirated into the analyte plasma. Because argon lines or OH bands (9) can occur in the region of interest via emission in the analyte plasma and obstruct measurements, they must be eliminated. This is accomplished by obtaining a background spectrum of the water. The first spectrum taken is that of magnesium radiation passing through the blank, water. This spectrum is denoted in Figure 7 by $I_O'(Mg + H_2O)$. The water spectrum $I_O'(H_2O)$ must be subtracted from $I_O'(Mg + H_2O)$ before the desired spectrum can be obtained. Therefore the two spectra are obtained in sequence and subtracted in computer memory. The resulting spectrum - $I_O(Mg)$ - is stored on disk for later data manipulation to obtain the absorbance spectrum.

Similarly for the $I_T$ measurement, magnesium is now aspirated into both plasmas with a lower concentration, typically 500 ppm, being aspirated into the analyte plasma. Emission from magnesium in the analyte plasma is still a

| | Source ICP | Analyte ICP |
|---|---|---|
| $I_0$ | Mg | $H_2O$ |
| | | $H_2O$ (background) |
| | $[\, I_0' (Mg + H_2O)\,] - [\, I_0' (H_2O)\,] = I_0$ | |

| | Source ICP | Analyte ICP |
|---|---|---|
| $I_T$ | Mg | Mg |
| | | Mg (background) |
| | $\left[ I_{T+E}' (Mg + Mg) \right] - \left[ I_E (Mg) \right] = I_T$ | |

$$\text{Absorbance} = \text{Log}_{10} \left( \frac{I_0}{I_T} \right)$$

Figure 7. Scheme for Obtaining $I_0$, $I_T$, and Absorbance.

problem - $I_E(Mg)$. As before two spectra were obtained, $I'_{T+E}(Mg + Mg)$ and $I_E(Mg)$. On subtraction the transmitted intensity $I_T(Mg)$ results and is stored on disk. By number crunching on the computer, the absorbance spectrum is obtained.

The concept discussed above is illustrated in Figure 8 with actual spectra. The spectra $I_O$, $I_T$ and Absorbance for magnesium and calcium are shown in this figure. Magnesium is viewed from 260 to 310 nm; calcium from 380 to 430 nm. The neutral atom and ion lines for these two elements are marked on the spectra. The neutral atom line for calcium at 422.7 nm is much weaker than the ion lines for calcium and thus was not observed. The spectra for $I_O$ and $I_T$ are shown in the upper portion of Figure 8 with the absorbance spectra obtained via data manipulation shown in the lower portion of this figure. This illustrates how "absorbance spectra" are obtained with the 1024-array.

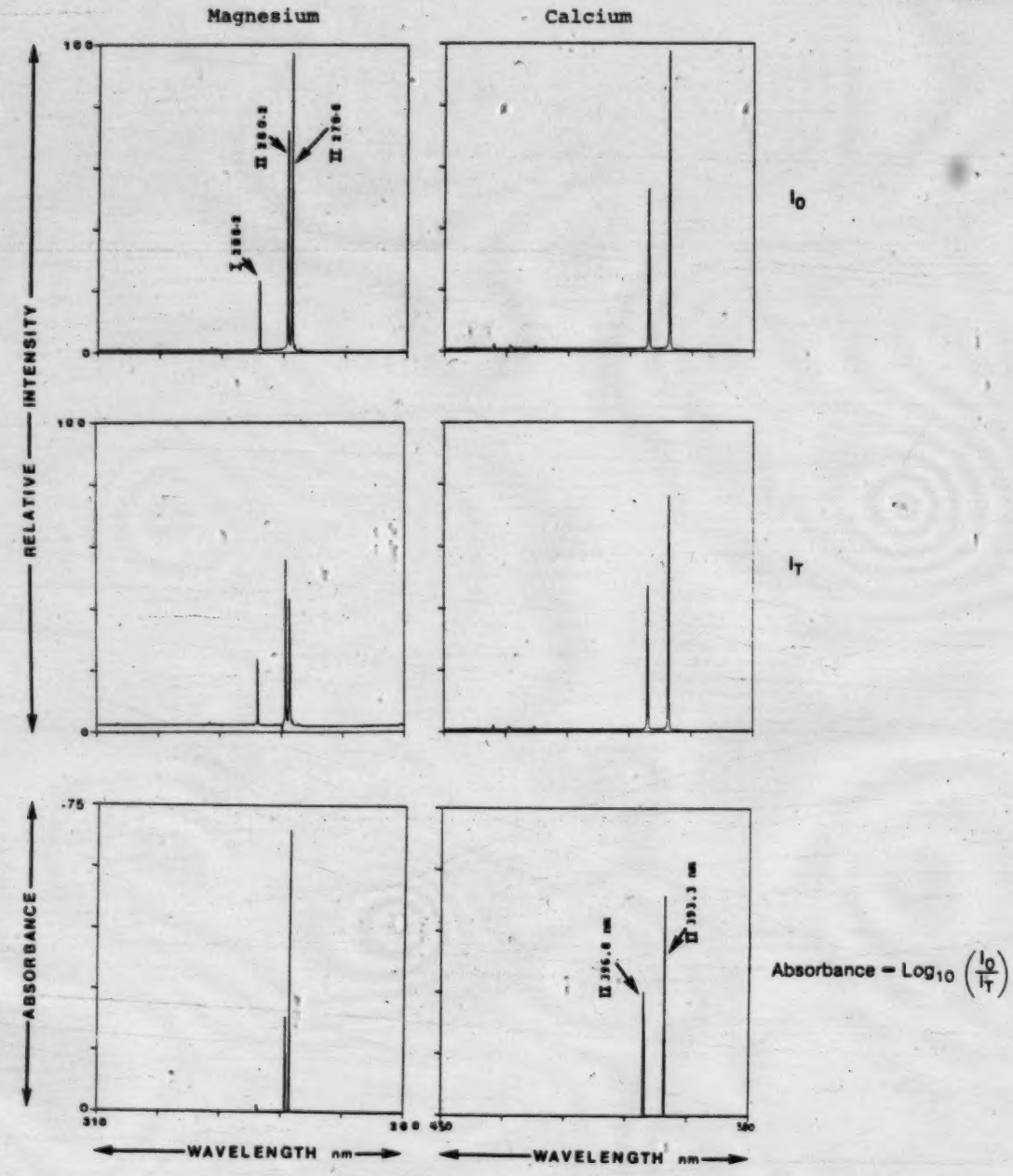



Figure 8. $I_0$, $I_T$, and Absorbance Spectra Obtained with a 1024-PDA Spectrometer for Mg and Ca.

# CHAPTER V

## RESULTS

In this preliminary study ICP-AAS as the analysis method with two plasmas has been shown to be successful. Calcium and magnesium were selected as elements for this study. Absorbance spectra as shown in Figure 8 were obtained.

### A. Calibration Curves

Calibration curves were measured. The source plasma was operated at 2.25 kW RF power and an analyte concentration of 10000 ppm while the analyte plasma was run at 1.5 kW RF power and an analyte concentration ranging from 10 ppm up to 1000 ppm. Absorbance values were taken from absorbance spectra similar to those in Figure 8 at the most sensitive line, in both cases the ion line, for the two elements studied. The calibration plots for Mg II line at 279.5 nm and Ca II at 393.3 nm are shown in Figures 9 and 10.

These plots are linear up to the high concentration end where they curve off towards the concentration axis. This may be the result of scattering or fluorescence of the signal intensity at the higher concentration levels in the analyte plasma. Indeed this must be investigated as atomic fluorescence (AF) can also be used as a means of obtaining ground state populations.

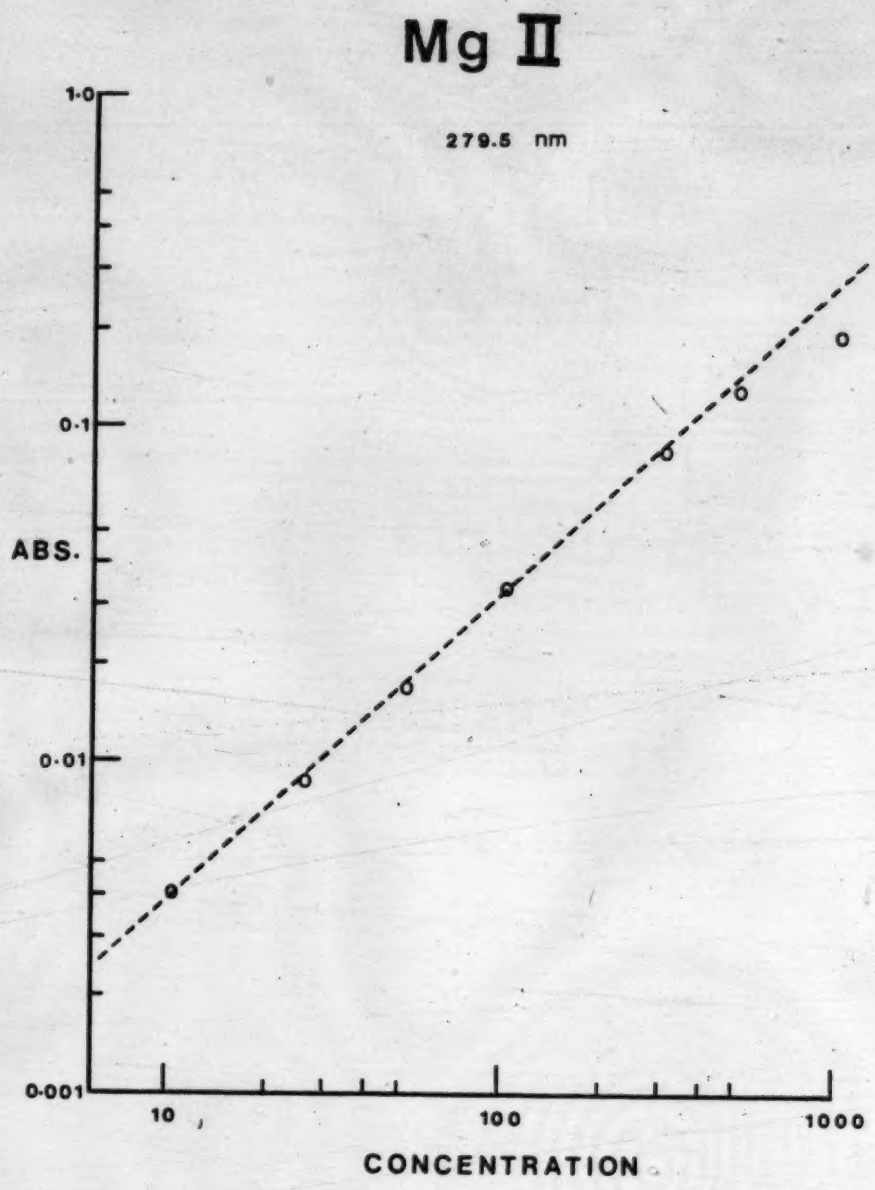



Figure 9. Calibration Curve for Mg II 279.5nm.

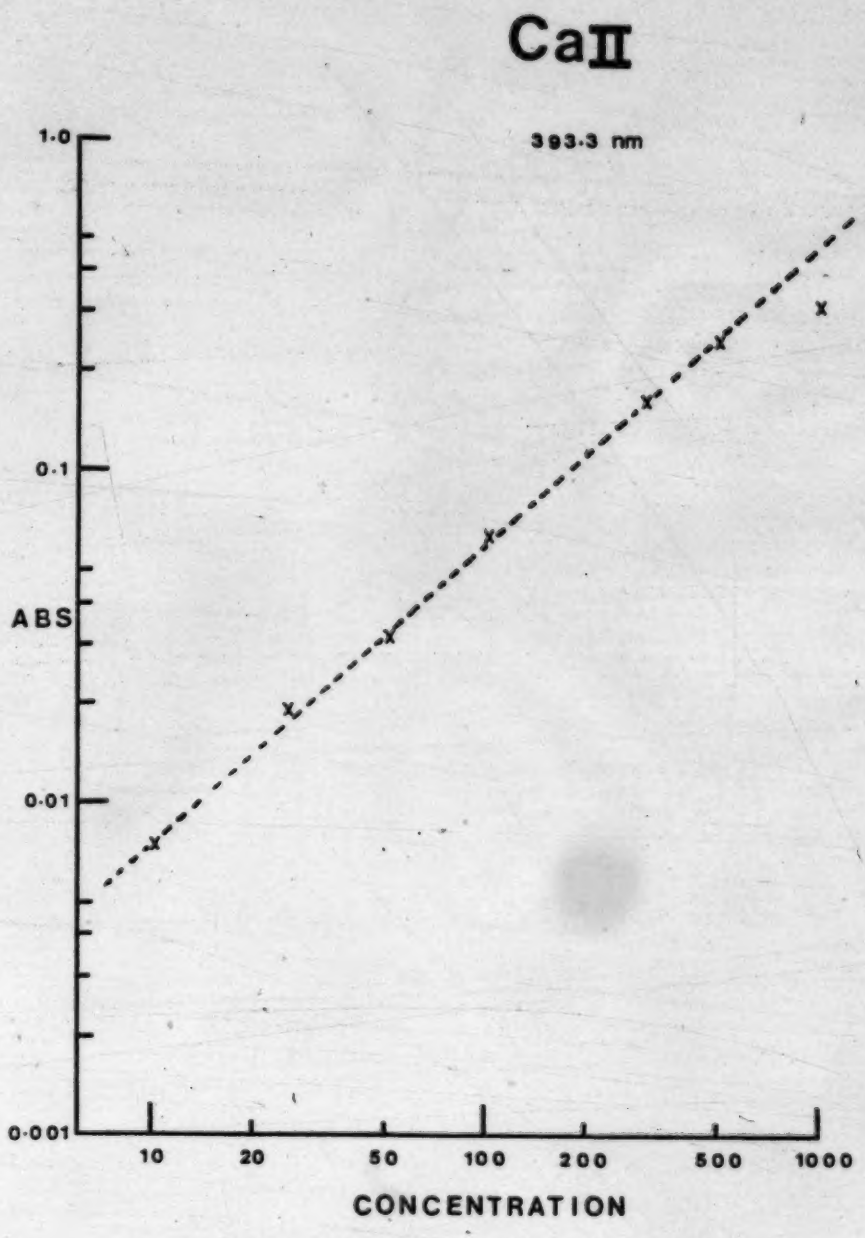



Figure 10. Calibration Curve for Ca II 393.3nm.

B. Absorbance versus Emission

1. Effect of Power

A study was conducted in which both absorption and emission spectra were taken back-to-back to serve as an intercomparison. The relative intensity, be it absorbance or emission signals, of the analyte species was plotted against the forward power with the source plasma fixed at 2.25 kW. At lower powers both absorption and emission signal intensities increased with increasing power. Eventually the ground state population reached a maximum and beyond this point the curve decreased in relative intensity.

This observation is illustrated in Figure 11. Absorbance reached a maximum for the ground state population at a lower RF power in the analyte plasma than emission. After this maximum the absorbance signal falls off in intensity while the emission continues to rise. The emission intensity appears to level off or possibly reach a maximum at a much higher forward power in the analyte plasma.

This observation may be the result of the population of excited states being filled at an earlier power for the absorbance signal compared to the emission signal. At low powers the plasma is physically smaller than at higher powers, but beyond a power setting of 1.5 kW, the physical size of the plasma has reached its limit - a limit set by the torch body. At this point further excitation of atoms only proceeds to fill the path length of the plasma to a greater degree. More excited atoms result in the analyte

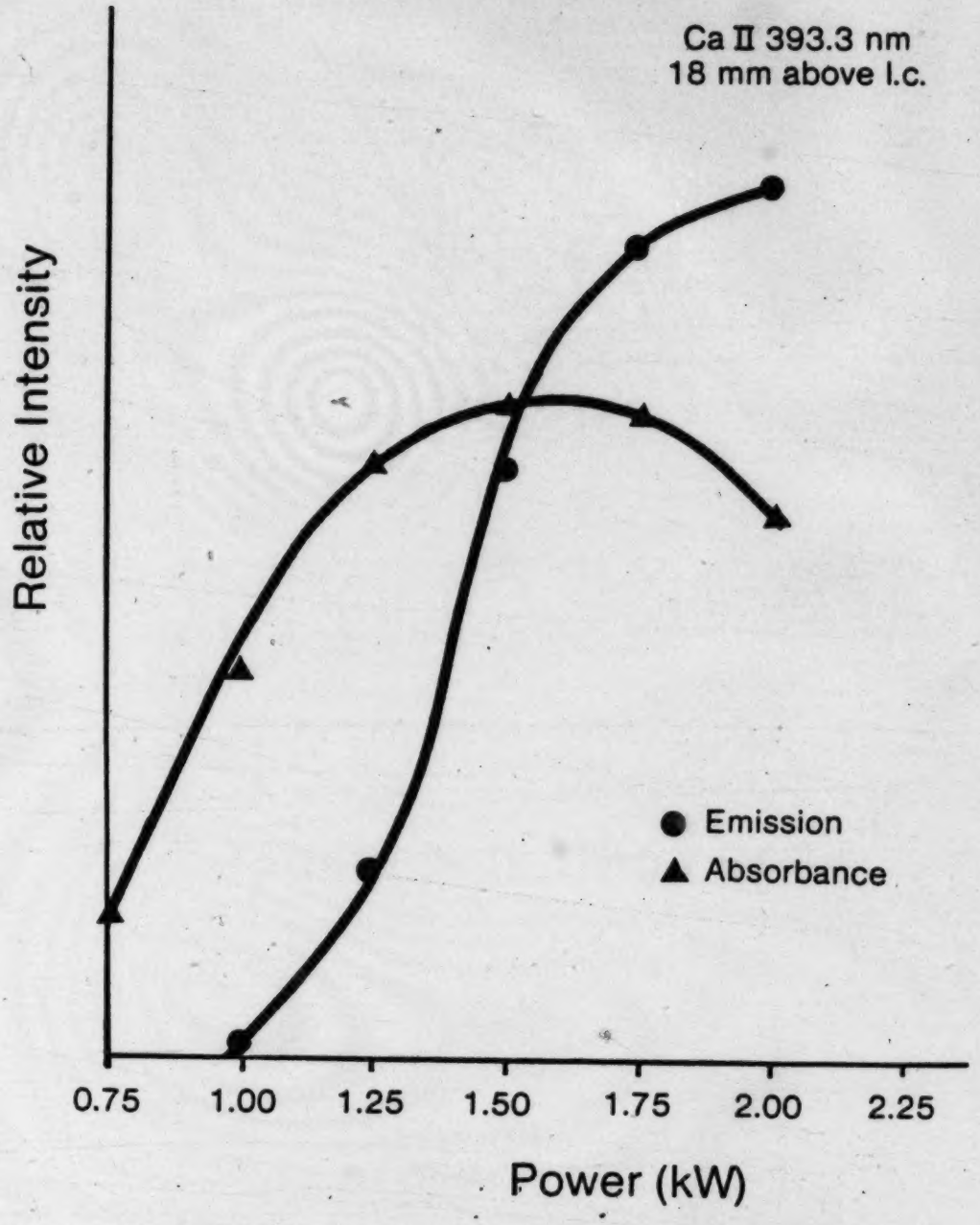



Figure 11. Comparison of Emission and Absorbance Intensities versus Forward Power at the Analyte Plasma for Ca II 393.3nm.

plasma at higher powers but are confined to the same path length in the plasma. As the radiation from the source plasma can only be absorbed by a limited number of excited atoms in the analyte plasma, a decline in the absorbance signal is observed when the radiation must pass through this higher density of excited atoms. The emission, however, still tends to increase with increasing power as seen in Figure 11.

2. Effect of EIE's

Much work has been done with easily ionizable elements (EIE) (10,27-36) and their effect on the intensity of analyte species in the plasma. A comparative study was carried out here with the two ion lines of calcium in the presence of various elements under the category of easily ionizable elements and in the absence of this concomitant. The absorbance and emission results are shown in Figure 12. As similar effects are observed one is lead to believe that the effect of EIE's on analyte species is largely due to a volatilization interference, that is, it is expected to occur in the transport delivery step.

C. Conclusions

Atomic absorption measurements have been found to be successful with the dual plasma setup proposed. This is largely due to the ICP being such a high thermal energy source. This allowed absorption to be measurable for both neutral atom and ion species. With a lower energy excitation source

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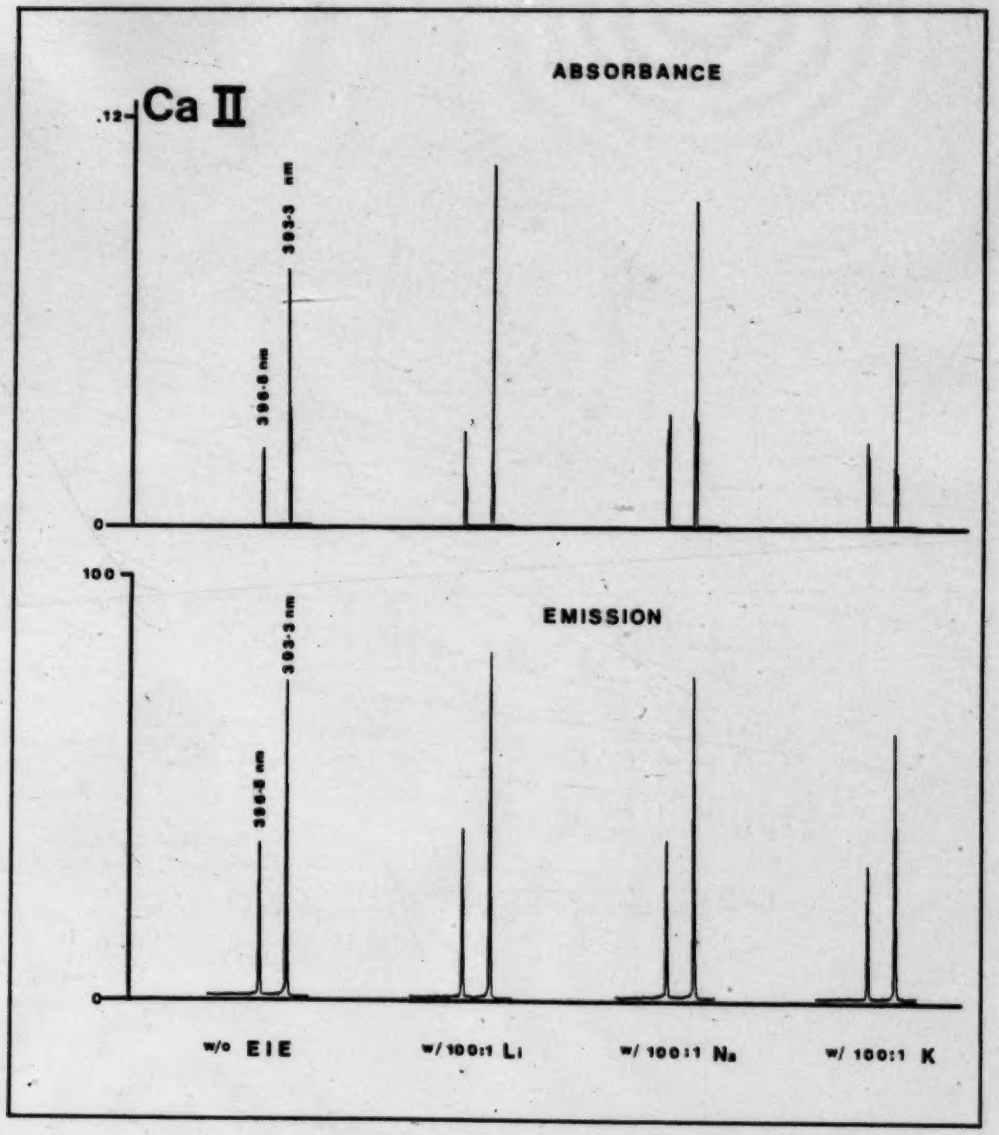



Figure 12. Effect of Different EIE's on Absorbance and Emission Intensities for the Calcium Ion Lines.

such as the HCL, only neutral atom absorbance can be measured. As well the operating conditions in the plasma must be maintained at a level where the emission does not swamp out the desired absorbance. With a source such as the MIP only argon species are readily measurable. The ICP wins out on all counts and is most suitable for adaptation to any type of measurement desired.

This has only been a preliminary study and further investigations must be carried out. Obviously other elements must be studied, besides just calcium and magnesium, as well as attempts to do multielement ICP-AAS simultaneously. A better understanding of plasma characteristics is expected when more detailed work on the effects of RF power at the analyte plasma on absorbance is measured. By altering each parameter separately in the plasmas an ideal set of operating conditions can be obtained. This will also aid in determining how each parameter affects the outcome of the absorbance.

As stated previously atomic fluorescence must be investigated as another means of measuring ground state populations. Then the three methods AE, AA and AF can be intercompared in the ongoing search toward the final goal - complete understanding of the inductively coupled plasma.

Thus the ground work has been laid for absorption analysis with a dual plasma setup. As a preliminary study the analyses end here but more work is hoped and expected to come from this group and others. The author hopes that elucidation via ICP-AAS will be expanded in the future and

thus help gain insight in the ICP's used by routine laboratories for application purposes.

# Part II

# Inductively Coupled Plasmas For Multielement Analysis

# CHAPTER VI

## INTRODUCTION

### A. Method of Choice

'In recent years the functions of trace elements in the human body and environment are being recognized in the biomedical and environmental field even through the mechanism [sic, roles] concerning the behavior of trace elements in biological systems is not completely clear' (37). With this growing interest in the effects of trace elements on plant and animal metabolisms the need for an appropriate analytical technique arises. The ideal technique must be able to determine trace levels in these materials and others rapidly and economically and with sufficient sensitivity to accurately detect normal, trace and subnormal levels (38).

Traditionally environmental samples have been analyzed using such methods as wet chemistry, spectrophotometry, atomic absorption spectrometry, and spark emission spectrometry. The last technique is very rapid and is capable of multielement analysis, but lacks sufficient sensitivity to detect elements at levels less than 10 μg/g in the detection of low levels. Atomic absorption analysis with a flame is not hampered by this problem and is readily capable of detecting elements at the μg/g level. The disadvantage here is slow thoughput of samples due to single element monitoring.

Spectrophotometric procedures are time consuming and less specific than atomic absorption. Wet chemical procedures are also time consuming and, in general, only provide accurate analyses for the major elements.

B. Reasons for Choosing ICP-AES

Inductively coupled plasma - atomic emission spectroscopy (ICP-AES) is now rapidly replacing these older methods of analyses. The advantage of ICP-AES over other atomic emission methods such as dc arc or solution-rotating disk optical emission spectroscopy have been covered in detail by other authors (37-43). Specifically, the excellent detection limits (at the ppb level for most elements); the multi-element capabilities; the accuracy and precision, especially at trace levels, due to the improved sensitivity and detection limits and to decreased matrix interference; the long linear dynamic range, allowing determination of trace and major constituents in the sample without dilution; absence of chemical interference; high speed with automatic sample input; long term analytical stability; and minimum operator expertise in computer controlled instrumentation are the factors which make the ICP so attractive as an emission technique.

In ICP-AES analyses the digested or extracted sample is presented as a liquid. Therefore the sample preparation technique employed must be capable of giving quantitative recovery for all of the constituents with minimum contami-

nation (38,40,44). The nebulizer used for sample transport places certain restraints on the sample, ie. the glass construction of the nebulizer precludes the presence of hydrofluoric acid in the digest and in order to avoid errors introduced by fluctuations in nebulizer performance, variations in the acid content for both samples and standards must be minimized (39,40,44,45).

C. Plasma Excitation

The operating principles for an ICP are discussed in detail by Fassel and Kniseley (46). Put simply, a plasma is formed when argon flowing through a quartz tube within an oscillating magnetic field is "seeded" by electrons from a Tesla coil. The plasma formed has an excitation temperature in the 5000K range (25).

The ICP is an optically thin source. This means there are few unexcited atoms in the optical path to reabsorb the emitted radiation so self-reversal, as seen in dc arc, ac spark and flame sources, is rarely encountered. This results in large linear dynamic ranges, typically four to six orders of magnitude, for the determination of concentration (47).

D. Sample Preparation

1. Pitfalls

There are two areas in which sample preparation is critical. The first is quantitatively recovering the analyte. Processes such as incomplete leaching, volatilization, absorp-

tion and precipitation can contribute to poor recoveries.

The second cause of problems is the behavior of the analyte in a given matrix in the instrument. The sample matrix can affect the environment of the flame or plasma and compensation for matrix effects is necessary to achieve accurate results.

2. Plant Tissue

Most analytical procedures for determining trace elements in biological and other organic materials require that the organic matrix be completely destroyed before analysis (37-44,47-53). Both wet and dry ashing techniques are commonly employed for matrix destruction (52), with the latter being preferred by most analysts because of convenience. The general procedure is to ash 0.5 to 1.0 grams of oven dried (85$^{o}$C) tissue and dissolve the ash in 10 to 20 ml of dilute acid (41,52,53).

Problems commonly associated with dry ashing include loss of elements by volatilization or bonding with the ashing container and formation of difficult to dissolve residual ash. Wet ashing is the method of choice for volatile metals. Ashing aids are sometimes employed with dry ashing. This may introduce unwanted metal contaminants. Similarly for wet ashing, catalysts can be a source of contamination or interference if the corresponding elements were being determined. Incomplete destruction of the matrix can cause clogging of the nebulizer used in ICP analyses.

A widely used wet ashing process which completely

destroys organic matter uses a combination of nitric, sulfuric and potentially explosive perchloric acids. This method is effective and safe provided:

a) the digest does not boil dry, which leads to volatilization losses and possible formation of spontaneously explosive perchloric esters;

b) digestion of samples having a fat and oil content greater than 50% is not attempted; and

c) the digestion is closely monitored to prevent charring which can also lead to volatilization losses and/or possible explosions.

Another wet ashing procedure uses nitric acid, heat and pressure in conjunction with a decomposition vessel to destroy most of the sample matrix. The primary disadvantage here is the sample size is limited to one gram of dry weight organic matter. Anything higher could be potentially explosive.

In this work dry ashing followed by acid dissolution was applied to plant tissue analyses.

3. Coal Samples

Coal is a heterogeneous material containing organic matter made up of carbon, hydrogen, nitrogen, oxygen, sulfur and mineral matter. Nearly every naturally occurring element known has also been found in coal or coal fly ash, most at very low or trace levels (54-62).

In view of the increasing national concern about the level of toxic elements in the environment, there is a need for

accurate, reliable analytical methods for measuring the concentration of trace elements in the complex matrix of coal which contributes to the pollution problems on burning or during the mining process when excessive amounts of coal dust are generated.

Coal samples must be oxidized prior to analysis to destroy the organic matter and then dissolved in an acid or base. Wet ashing with perchloric acid or by the use of oxygen or peroxide bombs are two such techniques. Another technique involves ashing the coal followed by fusion with fluxes such as carbonates, borates or hydroxides. Most of these procedures are slow and tedious requiring samples of about one gram and volatilization losses of some metals may occur. The fusion technique also precludes the determination of the particular cation used in the flux.

Dry ashing of the coal is quite popular. In this procedure powdered coal is ashed overnight in a muffle furnace set at 600° to 900°C. One-quarter gram samples of the ashed coal is acid bomb digested with aqua regia, hydrofluoric acid and boric acid. This technique was employed in the analysis of coal and more details involved with this method of sample dissolution will be discussed in the next chapter.

## CHAPTER VII

## ANALYTICAL PROCEDURE

### A. Instrumentation

The inductively coupled plasma (ICP) used in this study is a standard commercially available system consisting of a direct reading spectrometer and an ICP excitation source, Applied Research Labs (ARL) model 34000S ICP. Liquid samples are introduced into the plasma with a pneumatic nebulizer and spray chamber assembly. Specifications for the analytical system appear in Tables III and IV. Details on the instrument and operating conditions are provided in Table III. Analytical wavelengths for which the instrument is fitted and the average detection limits measured are given in Table IV. The spectrometer operation and data collection are computer controlled. An extended form of BASIC - ARLEB - is used for the calibration and analysis programs.

A periodic chart of the channels available on the ARL 34000S is shown in Figure 13. Thirty-four channels in all are available although only thirty-three elements are monitored since two cadmium channels exist - Cd II at 226.5 nm and Cd I at 228.8 nm.

The instrument must be calibrated for each sample type to be analyzed with accurate multielement solutions and matrix matched to reduce matrix effects. Flow charts of operation schemes typically performed with the ARL 34000S are shown in Tables II and III of the Appendix.

Table III. Specifications for the ARL 34000S ICP.

| Instrumentation and Operating Conditions | | |
|---|---|---|
| **Inductively Coupled Plasma** | | |
| RF Generator | : | Air-cooled, 0-2.5 kW continuous rating, operating at 27.1 MHz, crystal controlled to within 2000 Hz, pre-set autotuned 1200 W output power with 0 W reflected power. |
| Induction coil | : | Silver plated 3 turn copper tube, water cooled. |
| Plasma torch | : | Quartz with three concentric tubes for coolant gas, plasma gas and aerosol gas. |
| Nebulizer/spray chamber | : | Permanently aligned coaxial pneumatic nebulizer with computer controlled tip desalting; Scott-type coaxial spray chamber with direct aerosol injection. |
| Gas flows | : | LGS system, argon<br>coolant gas - 12 l/min<br>plasma gas -0.8 l/min<br>aerosol gas - 1 l/min<br>All gas flows regulated by triple regulation pressure valves with additional restriction by capillary orifices for coolant and plasma gases. |
| Enclosure | : | Fully enclosed by Faraday cages and all interlocked system. |
| Viewing height | : | 15 mm ± 1 mm, enclosure moving vertically on a 3-point mount and horizontally on a set of guides. |
| **Spectrometer** | | |
| Mount | : | 3 point cushioned mounting, 1.0 m Paschen-Runge, 3 section cast iron bolted vacuum spectrometer with argon purge to optics and plasma. |
| Optics | : | 1080 grooves/mm interferometrically ruled quartz blank replica grating blazed at 600 nm. Range:175-800 nm. Entrance slit 20 µm; exit slits 50 µm; primary lens quartz. Photomultiplier tubes for signal detection, 1 inch diameter; cathode biasing maximum of -970 volts and referenced to -100 volt ground. |
| Acquisition | : | Simultaneous capacitively stored charges with sequential conversion by a PDP 11/03 DEC computer with 32K memory. Software system is Applied Research Labs extended basic (ARLEB). Data outputted to an LA36 DEC hardcopy printer terminal. |

Table IV. Elements and Their Wavelenghs and Detection Limits on the ARL 34000S ICP.

HARDWARE CONFIGURATION 24-AUG-82 14:27:12

SCANNING PRIMARY SLIT (SAMI)
RX02 DISK
SYSTEM SERIAL DEVICES

MAIN CONSOLE ONLY ON SYSTEM

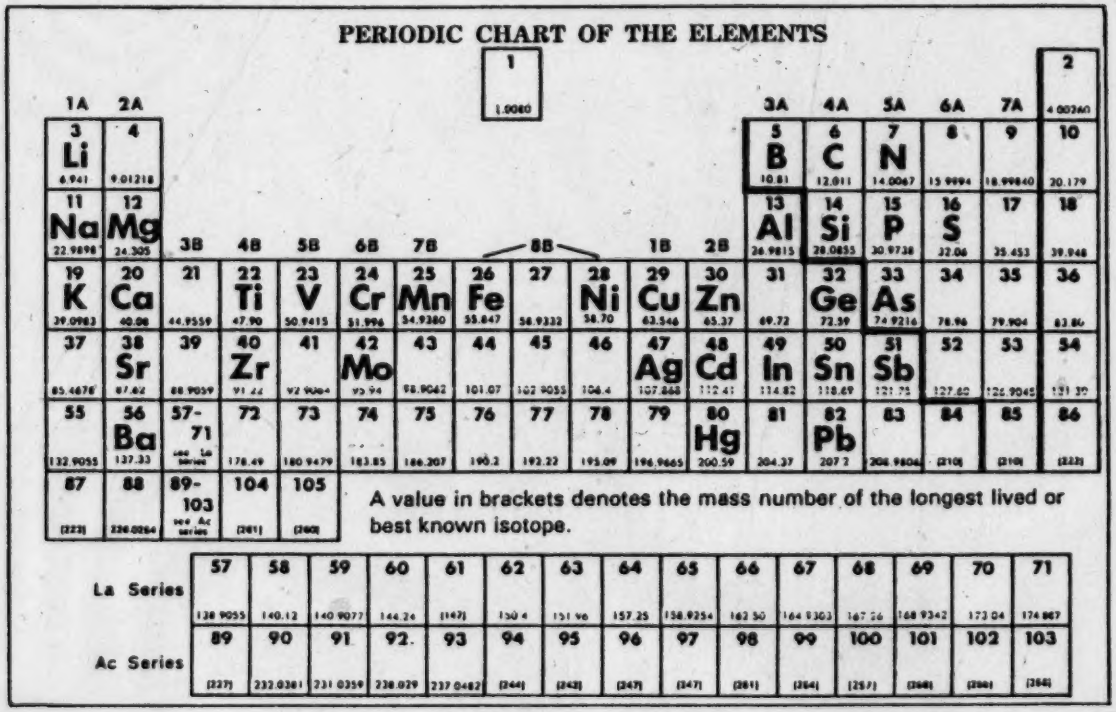
IS THE CONFIGURATION O.K. (Y/N)? Y

(P)RINT,(M)ODIFY SYMBOL TABLE? <CR> TO PROCEED? P

| CHANNEL NO. | ELEMENT | WAVELENGTH (NM) | ORDER | D.L. (PPM) |
|---|---|---|---|---|
| 1 | ZR | 343.82 | 1 | .00354 |
| 2 | SR | 407.78 | 1 | .00029 |
| 3 | BA | 455.40 | 1 | .00077 |
| 4 | NI | 231.60 | 2 | .0071 |
| 5 | AL | 237.34 | 2 | .07983 |
| 6 | B | 249.68 | 2 | .00371 |
| 7 | MN | 257.61 | 2 | .00179 |
| 8 | FE | 259.94 | 2 | .00256 |
| 9 | N | 174.27 | 3 | 0 |
| 10 | P | 178.29 | 3 | .0581 |
| 11 | S | 180.73 | 3 | .02662 |
| 12 | HG | 184.95 | 3 | .05356 |
| 13 | MG | 279.08 | 2 | .01663 |
| 14 | AS | 189.04 | 3 | .02153 |
| 15 | SN | 189.99 | 3 | .00995 |
| 16 | SI | 288.16 | 2 | .03377 |
| 17 | C | 193.09 | 3 | 0 |
| 18 | V | 292.40 | 2 | .00348 |
| 19 | NA | 589.59 | 1 | .0405 |
| 20 | MO | 202.03 | 3 | .00756 |
| 21 | CR | 205.55 | 3 | .00437 |
| 22 | SB | 206.83 | 3 | .02727 |
| 23 | GE | 209.53 | 3 | .05726 |
| 24 | CA | 317.93 | 2 | .00731 |
| 25 | ZN | 213.86 | 3 | .004 |
| 26 | CU | 324.75 | 2 | .00854 |
| 27 | AG | 328.07 | 2 | .00397 |
| 28 | PB | 220.35 | 2 | .00535 |
| 29 | LI | 670.78 | 1 | .00142 |
| 30 | TI | 337.28 | 3 | .00097 |
| 31 | CD1 | 226.50 | 3 | .00298 |
| 32 | CD2 | 228.80 | 3 | .00424 |
| 33 | IN | 230.61 | 3 | .05473 |
| 34 | K | 766.49 | 1 | .09404 |

DETECTION LIMIT MULTIPLIER TO USE AS LOWER ANALYTICAL LIMIT 5
INSTRUMENT GRATING NO. 1080
THIS IS A VACUUM SPECTROMETER

Figure 13. Periodic Chart Showing Only the Elements Available on the ARL 34000S ICP.

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For each sample type a separate TASK file must be generated. The program TASK creates a data file to establish the analytical conditions for the experiment, parameters which the operator designates appropriate to that file. Following this, the instrument must be calibrated with the program CAL, which analyzes standard solutions containing the known concentrations of elements set up under TASK. The measured intensity is used to calculate calibration curve coefficients for each element so that analyses via 'A', the analysis program, can apply these coefficients to allow calculation of unknown element concentrations. With quality control work, CAL is run once and then periodically normalized with NORM.

With the program NORM low and high standards for each element are run to determine the amount of change in the initial intensity readings and NORM updates the data in the calibration curves to compensate for any drift in sensitivity between analyses. Drift can result from environmental changes, instrumental changes and changes in the uptake rate. A single Meinhard nebulizer can vary from 2.8 to 3.2 ml per minute uptake rate during a four month period which can drastically affect results. All changes in parameters are adjusted with NORM to reflect these changes and the sample data, normalized on a day-to-day basis, is enticed to correspond to the stored calibration data. Only after this operation are analyses of samples carried out with the program A.

The ICP excitation box is detailed in Figure 14. Some differences exist between this excitation box and a Plasma-Therm excitation box which is used throughout the laboratory. These include:

a) A torch which is fully enclosed in a Faraday cage with the spray chamber hanging fixed and rigid outside the cage.

b) Desalting capabilities in which a device is incorporated that can automatically inject (under computer control) a jet of water at the conclusion of each analytical cycle into the carrier argon stream to rinse the nebulizer tip.

c) A device to bubble the carrier argon through water prior to passing into the nebulizer in order to prevent the sample solution, which may collect in the argon channel of the nebulizer, from drying out during operation.

B. Preparation of Standards

Definition of a suitable set of multielement calibration standards is the starting point for an ICP-AES calibration scheme. However, this is still a difficult task as elements must be grouped in such a manner that they remain stable in solution for long periods of time, that interelement effects are minimized, and that they bracket the anticipated elemental concentration range for the unknowns. After some trial-and-error experiences, the required standards and their composi-

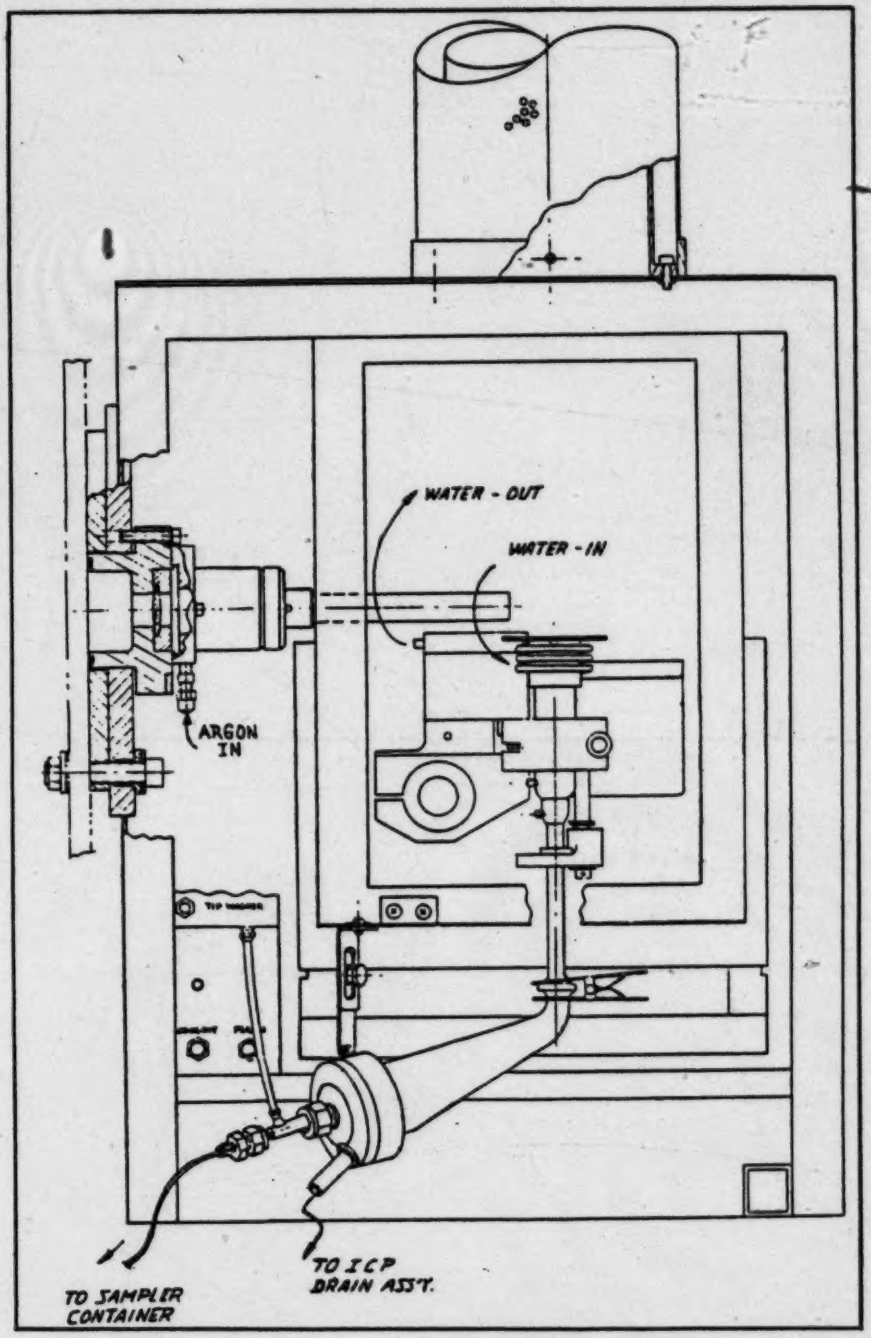



Figure 14. Diagram of ICP Excitation Box.

tions were found. Each standard solution contains the maximum number of compatible elements stable with time. It is equally important to match standards to samples for analysis as the sample matrix can provide a totally different set of interference problems.

An example of a matrix effect is illustrated in Table V - the effect of an easily ionizable element (EIE) on an analyte species, in this case, the effect of sodium on calcium and magnesium ion lines. A concentration of 2.5 mmolar in Ca and Mg, equivalent to 100 ppm and 60 ppm, was selected as the base concentration for addition of Na. Up to a 300 to 1 mmolar ratio excess of Na to that of Ca and Mg caused a depression in the emission intensity of the ion lines for these two elements. With a 300 to 1 mmolar ratio, the Mg intensity has dropped by 24% while the Ca signal intensity has been depressed by 16%. This depression in emission intensity for the ion lines was classically rationalized in analytical flame spectroscopy on the basis of a shift in the ionization equilibrium for analyte atoms (X), ions ($X^+$), and electrons ($e^-$).

$$X \rightleftharpoons X^+ + e^-$$

However, Blades (19) states:

> The classical interpretation in flames of a shift in the ionization equilibrium between analyte ion and neutral atom species does not seem to apply in the ICP. This is rationalized on the basis that the already high density of electrons in the plasma is not changed by the addition of EIE's ..... Clarification of the effect shows that the variability in the influence of EIE's

Table V. Classical Illustration of the Effect of an Easily Ionizable Element on the Ion Lines of Ca(393.3nm) and Mg(279.5nm).

| Effect of Sodium on Calcium and Magnesium | | |
|---|---|---|
| Sample | Ca | Mg |
| Ca 100 PPM - Mg 60 PPM No Na | 99.0 | 58.4 |
| With 10:1 Na:X | 96.9 | 56.3 |
| With 30:1 Na:X | 95.1 | 54.5 |
| With 100:1 Na:X | 92.2 | 50.7 |
| With 300:1 Na:X | 83.4 | 44.4 |
| 2.5 MMOLAR = 100 PPM Ca AND 60 PPM Mg | | |

reported by different workers is probably spatial in origin.

Further elaboration on the effect of EIE's is seen in a spatial study by Blades and Horlick (63).

Various authors have looked into the problems of preparing multielement calibration standards (38-42,58). Of these authors, McQuaker, Kluckner, and Chang (40) give the most elaborate scheme, which they used for analyses of environmental materials. They studied thirty elements - Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, Mg, Mn, Mo, Nb, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, V, Zn - with concentrations ranging from 0.010 to 500 ppm. They have also listed interelement interferences for twenty-three of these elements.

Munter, Grande, and Ahn (41) detail the set of calibration standards they used to analyze animal tissue and food materials. Their study involves fifteen elements - Ca, K, Mg, P, Al, Fe, Mn, Na, B, Cd, Cr, Cu, Ni, Pb, and Zn - with a concentration range of 10 to 3000 ppm. Two separate multielement standards have been used in their case. Lead and chromium would precipitate if they occurred in the same solution. Sodium, phosphorus and chromium were combined in one solution, with potassium dichromate and potassium dihydrogen phosphate as the sources for Cr and P because they will not interfere with the calibration for K which is contained in a separate standard.

The calibration scheme for four sets of multielement solutions is given in Tables VI through IX. These solutions

were prepared from single element stock solutions of 5000 ppm. For those multielement standards where elements required concentrations exceeding 1000 ppm, those elements were added in solid form, typically a salt, to the solution, with acid dissolution if necessary.

A general purpose multielement standard solution set, which was used here for water analyses and preliminary analysis of "unknowns", is given in Table VI. The standard solutions used for coal analysis are listed in Tables VII and VIII. Three additional elements - Ge, Hg, and Li - are given in the data listed in Table VII. These elements were eliminated from the second set of coal standards (Table VIII) as the levels for these elements in coal were found to be too low to be detectable. The second set of coal standards as presented in Table VIII is also a better representative set of calibration standards as it brackets better the elemental concentration ranges for the coal unknowns and NBS standards.

The final set of calibration standards listed in Table IX follows that outlined by Munter, Grande, and Ahn (41) with two exceptions - Ca and Mn - whose high standard concentrations were 750 ppm and 20 ppm as opposed to 3000 ppm and 100 ppm. The reason for this difference is the concentrations given by Munter, Grande, and Ahn (41) would saturate the photomultiplier tube (PMT) readout electronics used in this instrument and cause overranging to occur for both of these elements. This implies that with samples

Table VI. Calibration Scheme No. 1 - General Purpose.

All channels are monitored. All elements except Ba, N, S and Sr have upper concentrations of 100ppm. Ba and Sr have an upper concentration of 30ppm. N has concentrations of 264 and 79.2 ppm; S with concentrations of 37.5 and 11.25 ppm.

CALIBRATION SCHEME FOR GENERAL PURPOSE MULTIELEMENT STANDARD SOLUTIONS

| ELEMENT | GROUP NO. | STANDARD NUMBER and CONCENTRATION LEVEL, PPM | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
| Al | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| Ag | 7 | | | | | | | | | | | | | 100 | 30 | 0 |
| As | 4 | | | | | | | 100 | 30 | | | | | | | 0 |
| B | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| Ba | 2 | | | | 30 | | | | | | | | | | | 0 |
| C | 5 | | | | | | | | | 100 | 30 | | | | | 0 |
| Ca | 2 | | | 100 | 30 | | | | | | | | | | | 0 |
| Cd | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| Cr | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| Cu | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| Fe | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| Ga | 4 | | | | | | | 100 | 30 | | | | | | | 0 |
| Hg | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| In | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| K | 1 | 100 | 30 | | | | | | | | | | | | | 0 |
| Li | 1 | 100 | 30 | | | | | | | | | | | | | 0 |
| Mg | 2 | | | 100 | 30 | | | | | | | | | | | 0 |
| Mn | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| Mo | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| N | 5 | | | | | | | | | 264 | 79.2 | | | | | 0 |
| Na | 1 | 100 | 30 | | | | | | | | | | | | | 0 |
| Ni | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| P | 5 | | | | | | | | | 100 | 30 | | | | | 0 |
| Pb | 3 | | | | | 100 | 30 | | | | | | | | | 0 |
| S | 5 | | | | | | | | | 37.5 | 11.25 | | | | | 0 |
| Sb | 4 | | | | | | | 100 | 30 | | | | | | | 0 |
| Si | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| Sn | 3 | | | | | 100 | 30 | | | | | | | | | 0 |
| Sr | 2 | | | | 30 | | | | | | | | | | | 0 |
| Ti | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| V | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| Zn | 6 | | | | | | | | | | | 100 | 30 | | | 0 |
| Zr | 6 | | | | | | | | | | | 100 | 30 | | | 0 |

Table VII. Calibration Scheme No. 2 - Coal.
Twenty-eight elements studied under this scheme.

TASK FILE #TASK COAL ANALYSIS-MAJOR AND MINOR ELEMENTS 31-MAY-82

PRE-FLUSH TIME (SECONDS) 30
INTEGRATION TIME (SECONDS) 10
NUMBER OF INTEGRATIONS 6
TIP WASH

| ELEMENT | CONCENTRATION IN STANDARD | | | | | | |
|---|---|---|---|---|---|---|---|
| | # 1 | # 2 | # 3 | # 4 | # 5 | # 6 | # 7 |
| AL | 0.0000 | 150.00 | 500.00 | | | | |
| AS | 0.0000 | 15.000 | 50.000 | | | | |
| B | 0.0000 | 30.000 | 100.00 | | | | |
| BA | 0.0000 | 12.000 | 40.000 | | | | |
| CA | 0.0000 | 90.000 | 300.00 | | | | |
| CR | 0.0000 | 30.000 | 100.00 | | | | |
| CU | 0.0000 | 15.000 | 50.000 | | | | |
| FE | 0.0000 | 60.000 | 200.00 | | | | |
| GE | 0.0000 | 30.000 | 100.00 | | | | |
| HG | 0.0000 | 15.000 | 50.000 | | | | |
| K | 0.0000 | | | 29.010 | 96.690 | | |
| LI | 0.0000 | 15.000 | 50.000 | | | | |
| MG | 0.0000 | 30.000 | 100.00 | | | | |
| MN | 0.0000 | 15.000 | 50.000 | | | | |
| MO | 0.0000 | 15.000 | 50.000 | | | | |
| NA | 0.0000 | | | 497.70 | 1659.0 | | |
| NI | 0.0000 | 15.000 | 50.000 | | | | |
| P | 0.0000 | 15.000 | 50.000 | | | | |
| PB | 0.0000 | | | | | 15.000 | 50.000 |
| S | 0.0000 | | | | | 16.860 | 56.190 |
| SB | 0.0000 | | | | | 15.000 | 50.000 |
| SI | 0.0000 | | | 303.90 | 1013.0 | | |
| SN | 0.0000 | | | | | 15.000 | 50.000 |
| SR | 0.0000 | | | | | 9.0000 | 30.000 |
| TI | 0.0000 | | | | | 26.330 | 87.780 |
| V | 0.0000 | | | | | 30.000 | 100.00 |
| ZN | 0.0000 | | | | | 15.000 | 50.000 |
| ZR | 0.0000 | | | | | 30.000 | 100.00 |

NO SPECTRAL CORRECTION DATA IN TASK FILE

Table VIII. Calibration Scheme No. 3 - Coal. Twenty-five elements under study at more representative concentration ranges than those given in Table VII.

TASK FILE #TASK 25 MAJOR AND TRACE ELEMENTS IN COAL 14-JUN-82

PRE-FLUSH TIME (SECONDS) 30
INTEGRATION TIME (SECONDS) 15
NUMBER OF INTEGRATIONS 3
TIP WASH

| ELEMENT | CONCENTRATION IN STANDARD # 1 | # 2 | # 3 | # 4 | # 5 | # 6 | # 7 |
|---|---|---|---|---|---|---|---|
| AL | 0.0000 | 150.00 | 500.00 | | | | |
| AS | 0.0000 | 1.5000 | 5.0000 | | | | |
| B | 0.0000 | 300.00 | | | | | |
| BA | 0.0000 | 7.5000 | 25.000 | | | | |
| CA | 0.0000 | 90.000 | 300.00 | | | | |
| CR | 0.0000 | 3.0000 | 10.000 | | | | |
| CU | 0.0000 | 2.2500 | 7.5000 | | | | |
| FE | 0.0000 | 120.00 | | | | | |
| K | 0.0000 | 30.000 | 100.00 | | | | |
| MG | 0.0000 | 30.000 | 100.00 | | | | |
| MN | 0.0000 | 3.0000 | 10.000 | | | | |
| MO | 0.0000 | 0.7500 | 2.5000 | | | | |
| NA | 0.0000 | 1.5000 | 5.0000 | | | | |
| NI | 0.0000 | 3.0000 | 10.000 | | | | |
| P | 0.0000 | 15.000 | 50.000 | | | | |
| PB | 0.0000 | | | 1.5000 | 5.0000 | | |
| S | 0.0000 | | | 3.3700 | 11.240 | | |
| SB | 0.0000 | | | | | 1.5000 | 5.0000 |
| SI | 0.0000 | | | | | 300.00 | 1000.0 |
| SN | 0.0000 | | | | | 1.5000 | 5.0000 |
| SR | 0.0000 | | | | | 7.5000 | |
| TI | 0.0000 | | | | | 26.330 | 87.780 |
| V | 0.0000 | | | | | 7.5000 | 25.000 |
| ZN | 0.0000 | | | | | 15.000 | 50.000 |
| ZR | 0.0000 | | | | | 3.0000 | 10.000 |

NO SPECTRAL CORRECTION DATA IN TASK FILE

Table IX. Calibration Scheme No. 4 - Plant Tissue.

Fifteen elements made up for use in analysis of plant tissue, animal tissue and food material.

TASK FILE #TASK PLANT TISSUE ANIMAL AND FOOD MATERIAL 13-JUL-82

PRE-FLUSH TIME (SECONDS) 30
INTEGRATION TIME (SECONDS) 15
NUMBER OF INTEGRATIONS 3
TIP WASH

| ELEMENT | CONCENTRATION IN STANDARD | | | | |
|---|---|---|---|---|---|
| | # 1 | # 2 | # 3 | # 4 | # 5 |
| AL | 0.0000 | 20.000 | 100.00 | | |
| B | 0.0000 | 2.0000 | 10.000 | | |
| CA | 0.0000 | 150.00 | 750.00 | | |
| CD1 | 0.0000 | 2.0000 | 10.000 | | |
| CD2 | 0.0000 | 2.0000 | 10.000 | | |
| CR | 0.0000 | | | 2.0000 | 10.000 |
| CU | 0.0000 | 2.0000 | 10.000 | | |
| FE | 0.0000 | 20.000 | 100.00 | | |
| K | 0.0000 | 600.00 | 3000.0 | | |
| MG | 0.0000 | 200.00 | 1000.0 | | |
| MN | 0.0000 | 20.000 | | | |
| NA | 0.0000 | | | 20.000 | 100.00 |
| NI | 0.0000 | 2.0000 | 10.000 | | |
| P | 0.0000 | | | 100.00 | 500.00 |
| PB | 0.0000 | 2.0000 | 10.000 | | |
| ZN | 0.0000 | 2.0000 | 10.000 | | |

NO SPECTRAL CORRECTION DATA IN TASK FILE

where the Ca and Mn concentrations exceed the level set by the standards, serial dilution of the sample is necessary, which was the case in some of the samples analyzed.

C. Preparation of Samples

Sample preparation is often the slowest step of the analytical process in any laboratory. In order to fully take advantage of the speed of measurement of the inductively coupled plasma direct reader, a fairly rapid digestion procedure is needed. In this work the fastest method found was overnight dry ashing followed by acid dissolution prior to analysis by the ICP.

Whether the sample type is geological, agricultural, biological or environmental, two major factors are responsible for the lengthy sample preparation process. One factor is to obtain a representative sample and the other is to get the sample into solution form. The sample must be ground and thoroughly mixed. A small amount, typically a one-gram portion, undergoes some method of dissolution suitable for that particular sample type and which minimizes loss of the volatile elements.

The assays generated in this work included water samples, coal - mainly NBS standard reference materials, and plant tissues.

Water samples were analyzed as received without additional treatment. However, loss of some metals - Al, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, and Zn - has been found to occur upon

storage in Pyrex and Nalgene containers (64,65,65a). Methods for the storage and processing of water samples for trace metal analysis by atomic absorption spectrometry have been investigated (64,65). Loss of the above mentioned metals can be minimized at pH<1.5 with $HNO_3$ (64). This acidification method was not used on the water samples in this study because high purity $HNO_3$ was not readily available to the author.

Plant tissues were dry ashed overnight in a muffle furnace set at 485°C. The ash was then dissolved in 10 ml of 2N hydrochloric acid about one hour prior to analysis. The samples were analyzed in triplicate studying 1.00, 0.50 and 0.25 gram samples. This range of sample weights was used to bring the major elements - Ca, K, Mg and P - within the range set by the standards used.

Coal requires extensive chemical treatment prior to analysis. The organic material must be destroyed and the inorganic material dissolved in an appropriate solvent. The various operations must be carried out without loss of the volatile elements. The organic content of coal is totally destroyed with high temperature (600°C) ashing. The only major component lost with this technique is sulfur. The resulting ash can then be dissolved via one of several techniques. The techniques used in this work include: wet digestion with 1:3 $HNO_3$:HCl (aqua regia), 3:1 $HNO_3$:HCl (reversed aqua regia), and 1:1 $HNO_3$:HCl; fusion of the ash with excess NaOH at 900°C followed by dissolution of the

fused product with concentrated hydrochloric acid; acid bomb digestion with aqua regia/HF/$H_3BO_3$; and wet digestion with perchloric acid (55).

Problems exist with each of these techniques. Wet digestion with the various ratios of $HNO_3$-HCL mixtures gives incomplete dissolution of the sample. The technique of fusing the ash with NaOH at 900°C causes interferences for Na determination by the matrix. Digestion of ashed samples with perchloric acid requires a special "clean" hood for handling the perchloric acid.

Hydrofluoric acid is used in the acid bomb digestion to decompose the siliceous residue remaining after the digestion, but HF readily attacks glass and thus demands the use of teflon beakers. Removal of HF is mandatory when regular glassware is used in the ICP excitation box if one does not wish to degrade the quality of either the nebulizer or the torch. Boric acid converts the remaining HF to $BF_3$, but B determination is then not valid (56).

Of these techniques, the acid bomb digestion was found to be most suitable. A blank containing similar quantities of aqua regia/HF/$H_3BO_3$ must be prepared in the same manner as the samples undergoing analysis.

The samples were ashed at 600°C in a muffle furnace for 24 hours with stirring at one to two hour intervals to expose unashed coal. NBS SRM 1632 coal has a 13.5 + 0.2 percent ash content. Local coal samples used had percent ash contents ranging from 5% up to 15%. Approximately 0.25 grams of the

ash was transferred to the Teflon container of the bomb and 3 ml of aqua regia was added. The bomb was sealed and placed in a 105°C oven for 2 hours. After cooling 10 ml of 74% HF was added and heated in the bomb at 120°C for an additional half hour. Approximately 7.5 grams of $H_3BO_3$ was added to the cooled container and diluted to a final volume of 250 ml.

## CHAPTER VIII

## RESULTS AND DISCUSSION

### A. Introduction

In this study with the ICP/direct reader as an analytical tool, various samples were analyzed - coal samples, botanicals and water samples. Of these three sample types, coal was studied extensively via sample preparation techniques described previously and will only be dealt with in this section under the sample preparation technique found most useful - acid bomb digestion.

Botanicals were studied using only one method of sample dissolution. As more samples were studied in this group this section will be devoted mainly to the botanicals.

Water samples requiring no pretreatment were aspirated directly whenever samples were received.

Calibration curves will be inspected briefly first. The calibration curves under study are those obtained for two of the task files compiled.

### B. Calibration Curves

In each task file generated, the elements selected for study were set up using a three point calibration plot. Zero concentration, a high concentration representative of the sample to be analyzed, and an intermediate concentration for each element were the points selected for calibration.

All elements set at the same upper concentration value

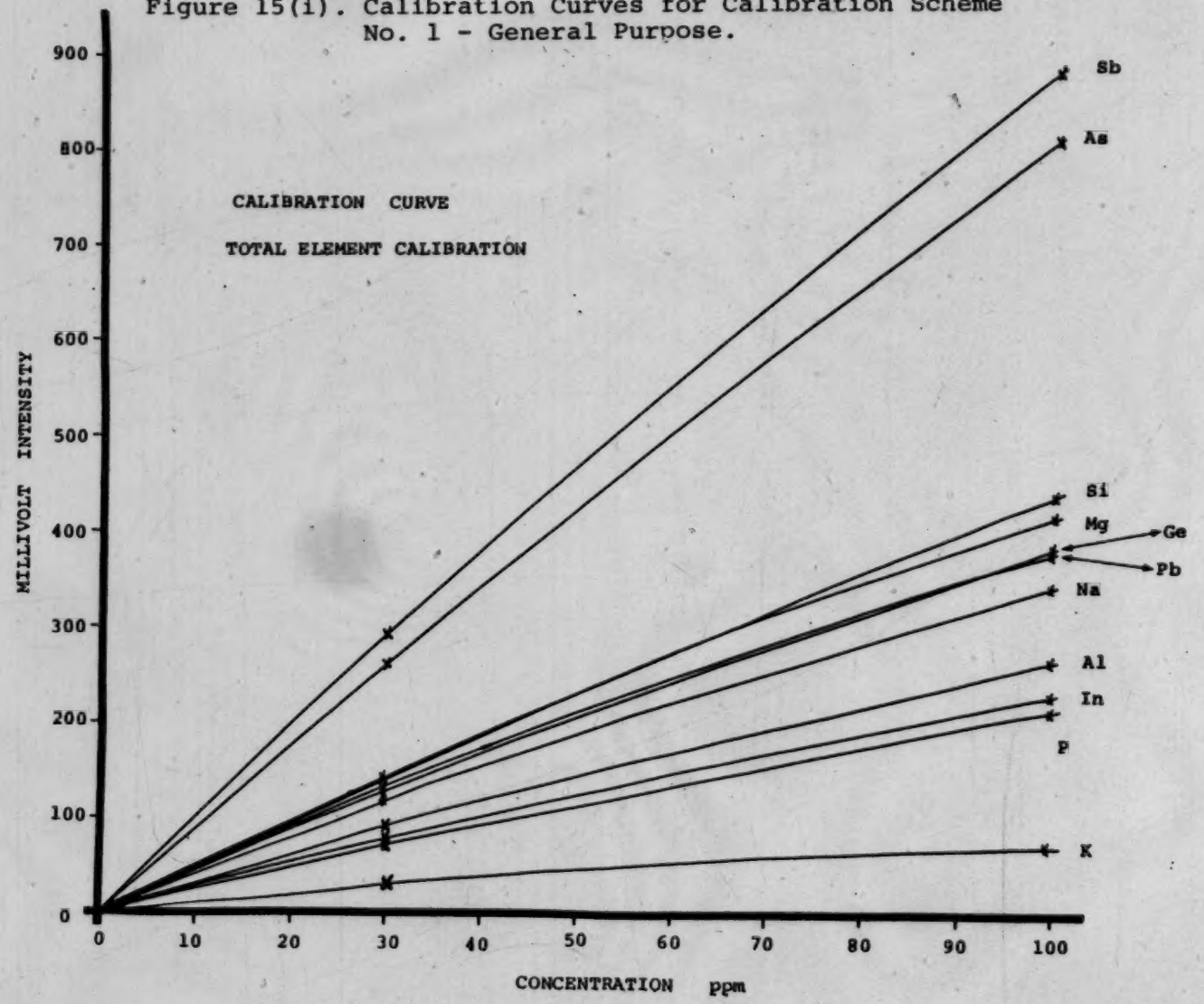
will not give similar emission intensities. This is illustrated in the calibration curves of Figure 15. This data is taken from the task file set up for general purpose work studying all channels. The high concentration is 100 ppm for all elements except Ba and Sr with high concentrations of 30 ppm and S at a high of 37.5 ppm.

Every element at the same concentration gives different photomultiplier (PMT) intensity readings. In Figure 15(i), the eleven elements all at 100 ppm high concentration, range in millivolt intensity from about 50 mV up to 900 mV. The millivolt maximum in Figure 15(ii) exceeds 3000 mV while in Figure 15(iii) approaches 15000 mV, one element approaching this limit is Sr at only 30 ppm.

This difference in millivolt intensity for different elements is due to the emission sensitivity characteristic of the wavelength with which the instrument is fitted. For example, the Ca II 393.366 nm line is the most intense Ca line, but the analytical wavelength of Ca II used with this instrument is the 317.933 nm line, which is sixty times less sensitive than the 393.366 nm line. This prevents the readout electronics of the PMT from excessive saturation and overranging problems at high concentrations of Ca which is typical of many sample types. Overranging still occurred for Ca II 317.933 nm with botanicals studied at one gram sample weight sizes.

Barium and strontium exist on the 34000S ICP as ion lines 455.403 and 407.771 nm. These are the most sensitive

Figure 15(i). Calibration Curves for Calibration Scheme No. 1 - General Purpose.



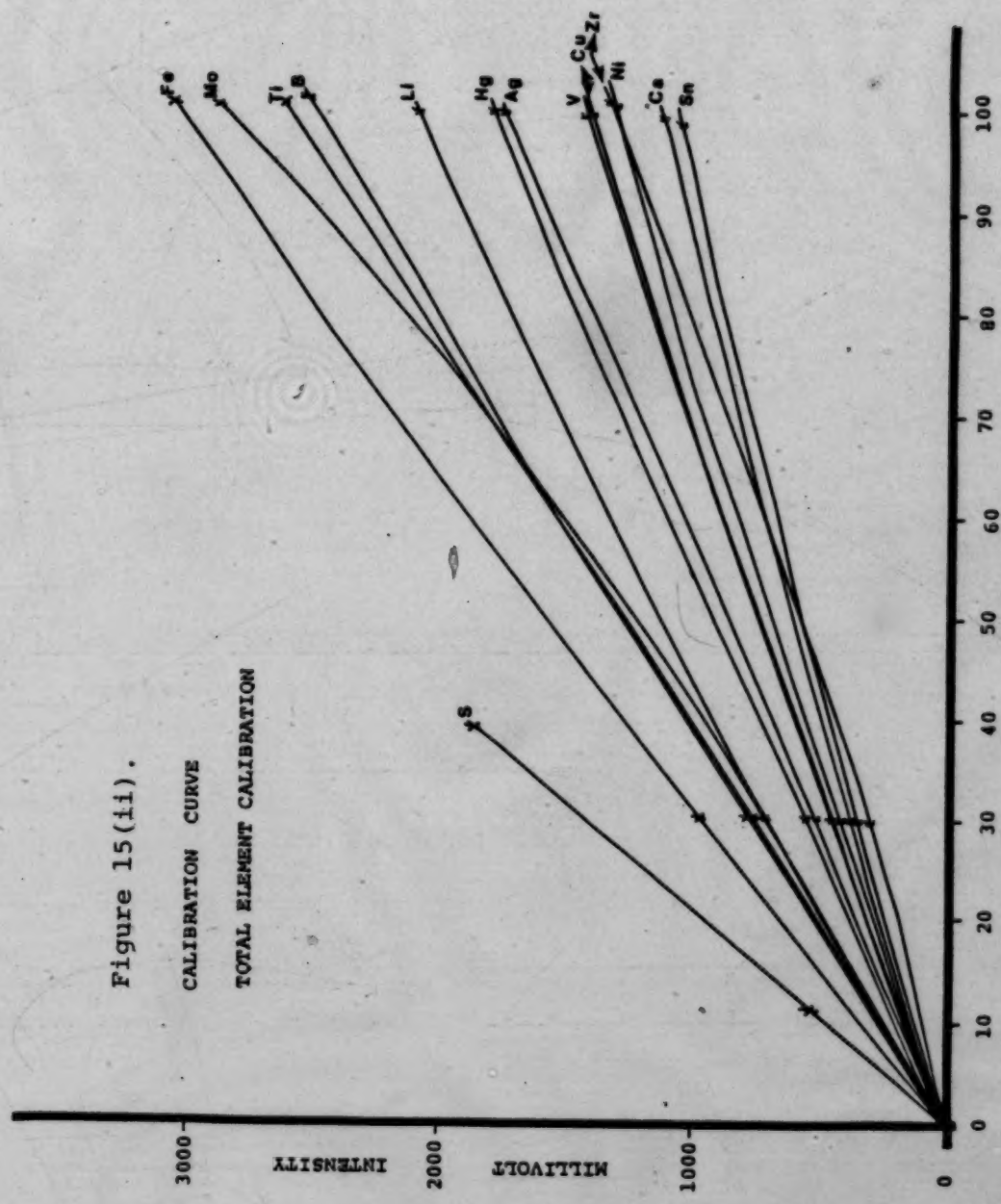
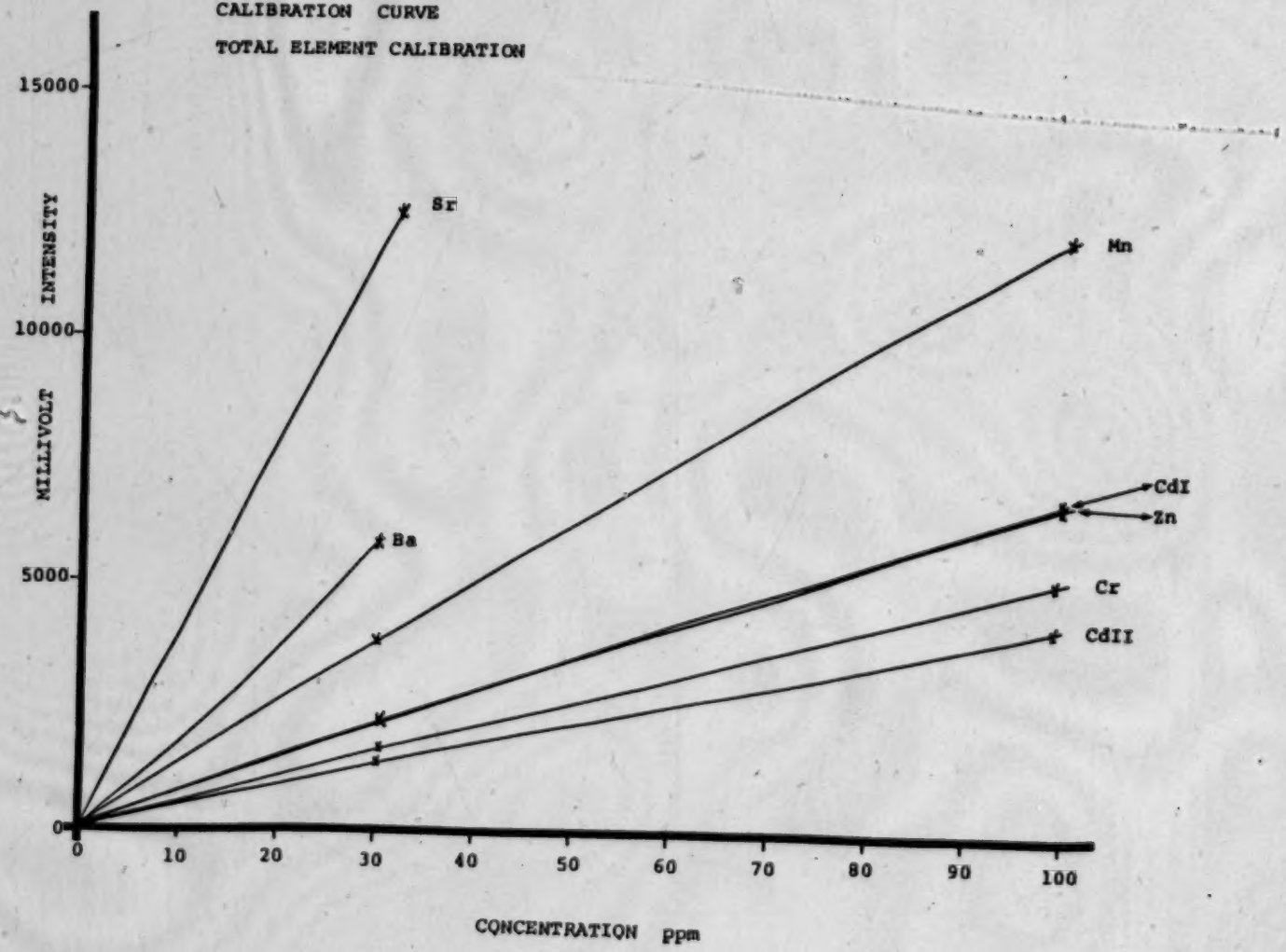

CALIBRATION CURVE
TOTAL ELEMENT CALIBRATION
INTENSITY
MILLIVOLT
CONCENTRATION ppm
Fe
Mo
Tl
B
Li
Hg
Ag
V
Cu
Zr
Ni
Ca
Sn
S
0
1000
2000
3000
10
20
30
40
50
60
70
80
90
100

Figure 15(ii).

Figure 15(iii).



lines for these two elements but since they normally occur at relatively low concentration levels in environmental samples and alloys, the most sensitive line was fitted into the instrument for each. Millivolt intensities exceeding approximately 14000 mV tend to saturate the readout electronics because they approach or exceed the biasing voltage of +15V. This occurs for Ba and Sr levels exceeding 30 ppm and thus this was the value (or somewhat lower) chosen as the maximum concentration level for these two elements.

Each element reaches readout saturation at different concentrations. For example, K in Table IX, the calibration scheme for plant tissue, animal and food material, is set at an upper concentration of 3000 ppm, but the millivolt intensity is only about 2000 mV. To approach saturation with K a concentration of 2.0% would be necessary assuming linearity. Another example would be Pb, as a concentration level of approximately 100,000 ppm would be required before saturation with this system.

These three calibration curves with concentrations up to 100 ppm show that the plots are linear for the three point calibration curves. Calibration curves for the elements studied in coal are also linear (see Figure 16). Their concentrations range from 5 to 1000 ppm as the upper concentration value for that particular element. Similarly, those for the botanicals, using the task file entitled 'Plant Tissue, Animal and Food Material' were also linear.

The calibration plots for coal analyses, Figure 16, are

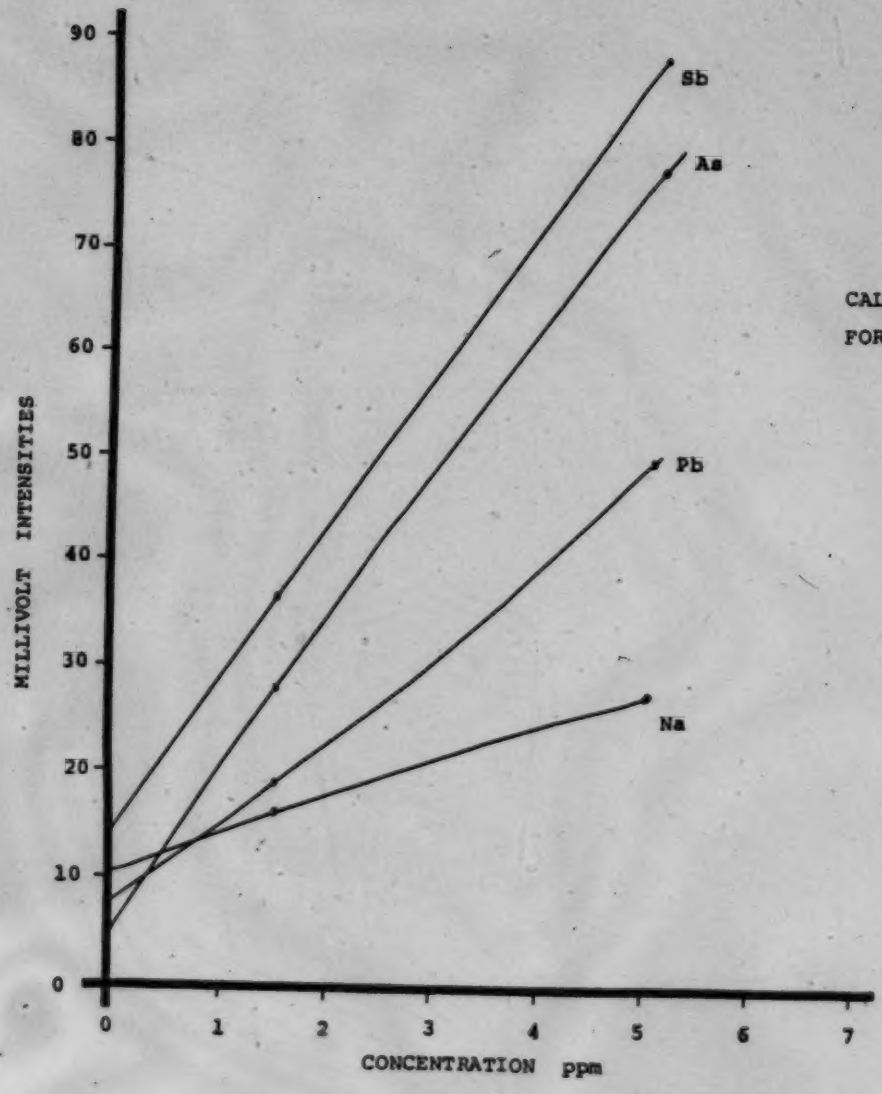



Figure 16(i). Calibration Curves for Calibration Scheme No. 3 - Coal.

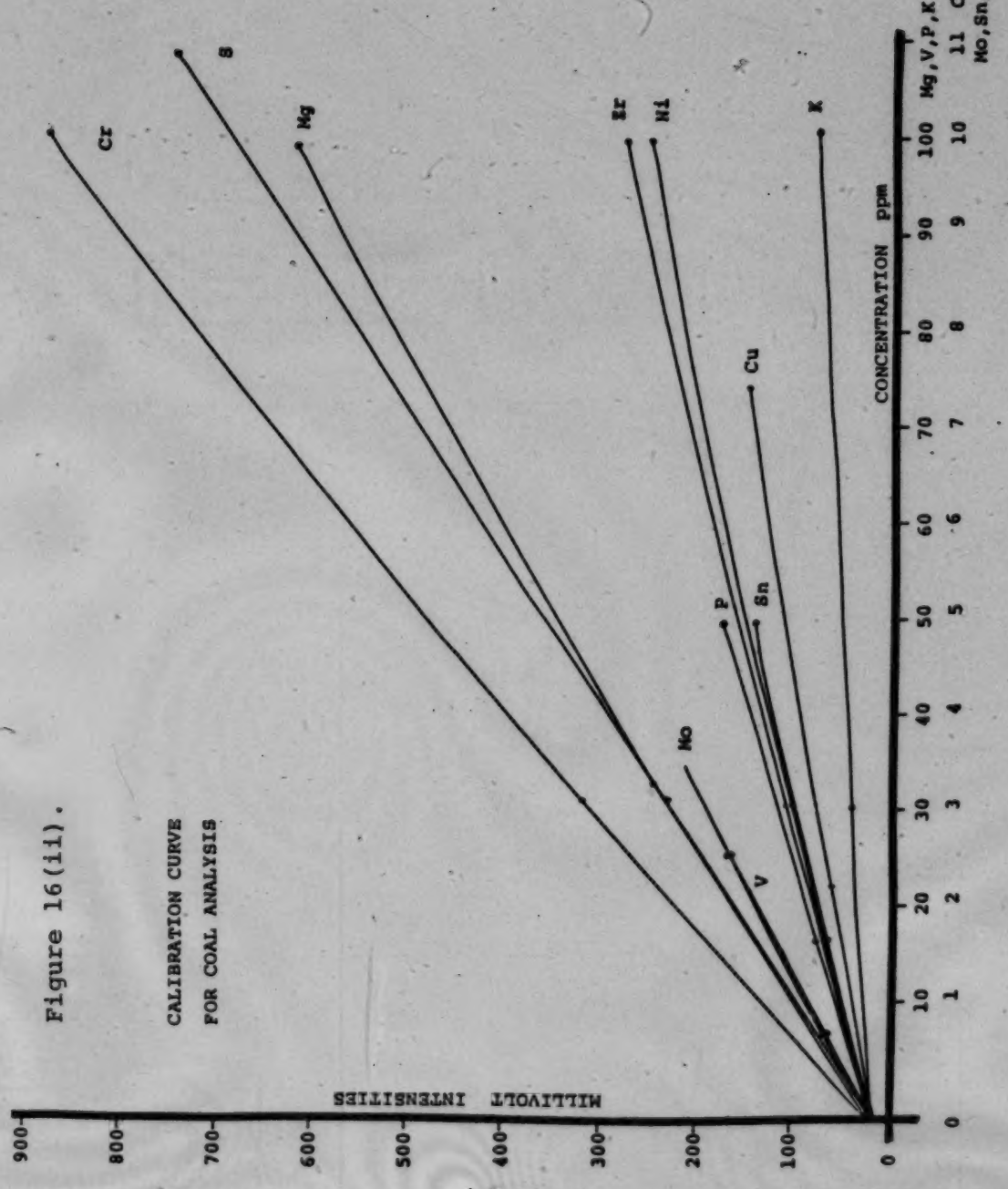
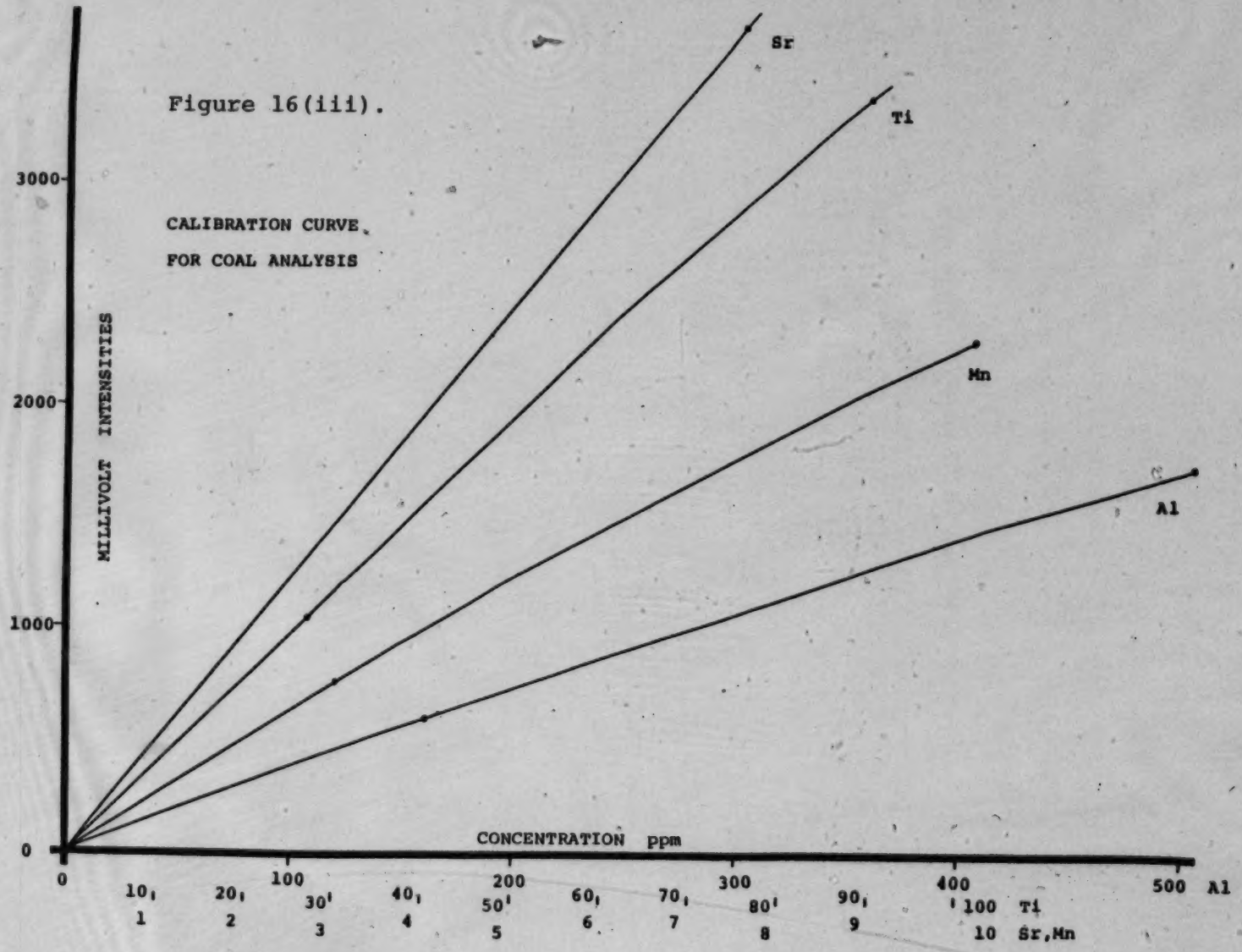



Figure 16(ii).

CALIBRATION CURVE
FOR COAL ANALYSIS

Figure 16(iii).



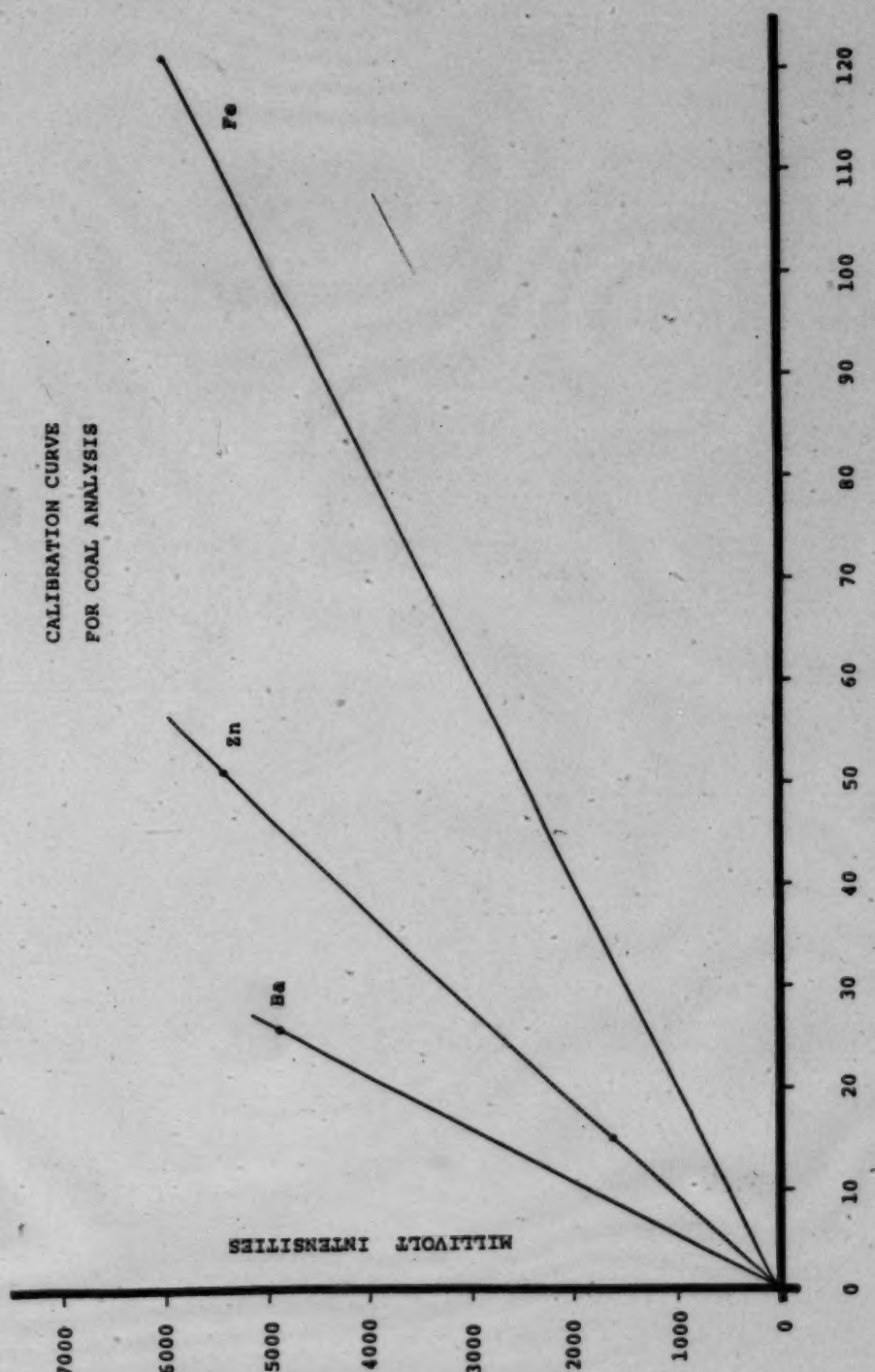
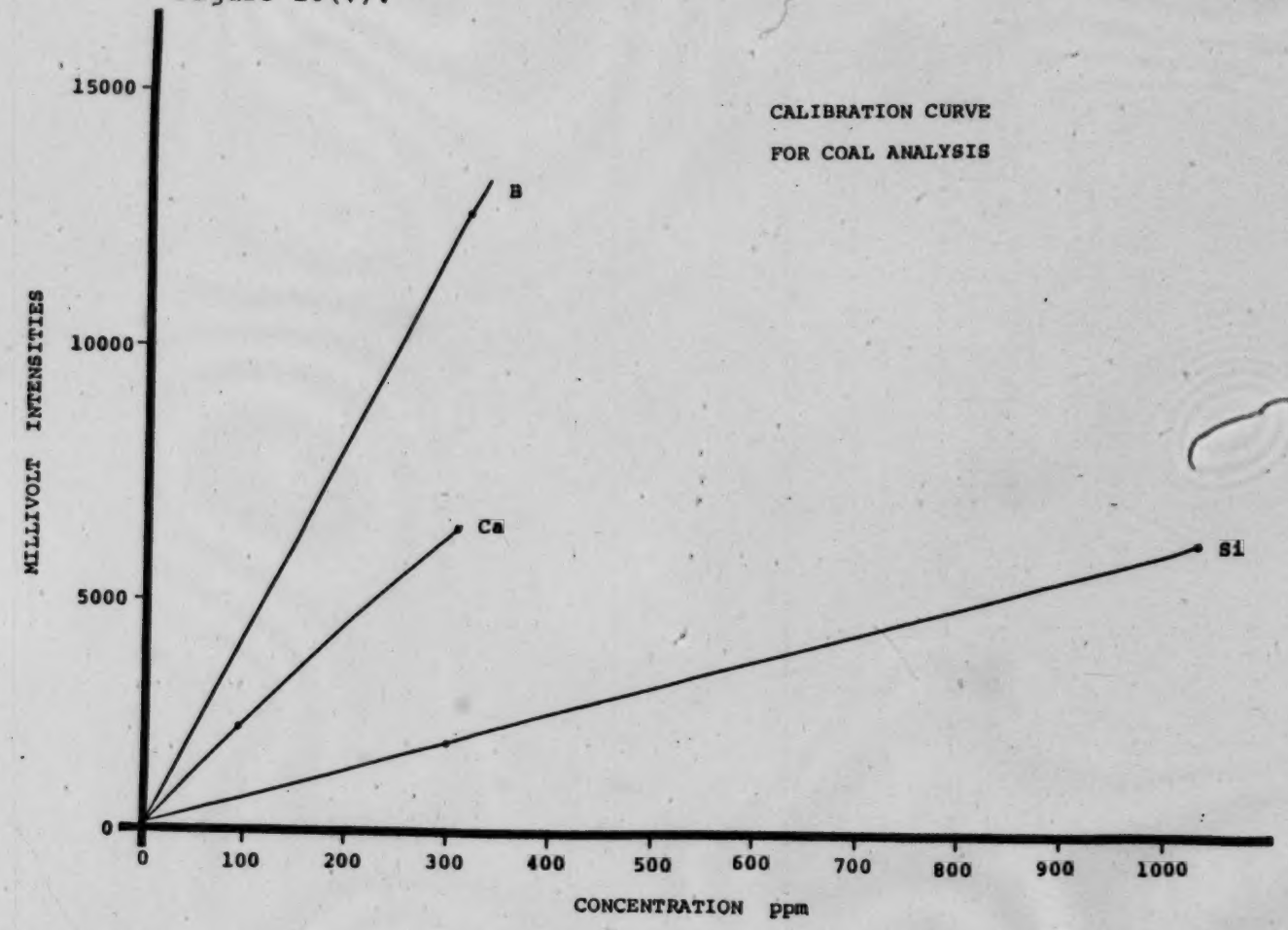

CALIBRATION CURVE
FOR COAL ANALYSIS
MILLIVOLT INTENSITIES
CONCENTRATION ppm
Fe
Zn
Ba
0
1000
2000
3000
4000
5000
6000
7000
0
10
20
30
40
50
60
70
80
90
100
110
120

Figure 16(iv).

Figure 16(v).


CALIBRATION CURVE
FOR COAL ANALYSIS
MILLIVOLT INTENSITIES
15000
10000
5000
0
B
Ca
Si
0
100
200
300
400
500
600
700
800
900
1000
CONCENTRATION ppm

those for the second task file entitled '25 Major and Trace Elements in Coal' (Table VIII). This set was found to be more representative for coal. For instance, some elemental concentrations were decreased, as compared to the concentrations given in Table VII, to more accurately approach the actual levels in coal - As, Ba, Cr, Cu, Fe, Mn, Mo, Na, S, Sb, Sn, V and Zr - while B was increased in concentration. Boron was eventually not analyzed in coal because the boric acid added in excess to the acid bomb digestion to remove HF and any silicate fluoride precipitates interferes with the measurement of boron.

C. Coal Analysis

Coal requires extensive preparation prior to aspiration into the plasma/direct reader for analysis. The coal must first be ashed. Various dissolution techniques were previously discussed. The one giving the best results was acid bomb digestions using aqua regia/hydrofluoric acid/boric acid. The analytical results for the National Bureau of Standards (NBS) coal and coal fly ash (SRM 1632 and 1633) appear in Table X. The values obtained by this method are compared to either NBS values or values found in the literature (56-62). Literature values were used in cases, such as sulfur, where NBS values were not available.

The values agree favorably with the exception of sulfur, which is approximately 10% of the actual value quoted in literature. Sulfur is lost for several reasons. High

temperature (600°C) ashing for 24 hours causes some loss of sulfur. Hydrogen sulfide ($H_2S$) gas evolution was also noted on opening the bomb after heating.

Otherwise, on the whole, the twenty-two elements listed gave good agreement to accepted values. Boron was excluded from the list because the boric acid added saturated the readout electronics of the PMT to such a degree that even with background correction, no value could be accurately obtained for this element. Molybdenum and nickel were not at levels high enough to be observed and thus were also excluded from Table X.

The coal analysis was used as a starting point for checking reliability with the instrument. Accuracy was good. In this study no further work was done on coal samples. Another sample type - botanicals was chosen for further characterization.

D. Analysis of Botanicals

Botanicals have been studied in great detail with the inductively coupled plasma (37-44,48-53,66). Three samples of National Bureau of Standards (NBS) orchard leaves, spinach and tomato leaves were analyzed after the dry ashing/acid dissolution procedure described in the previous chapter. NBS standards were chosen for initial analyses to check on the performance of the ICP spectrometer. Additional local plant material was analyzed as well. Whenever a series of these plant tissue ashes were analyzed, a comparable NBS

Table X. Analytical Results for NBS SRM's 1632 and 1633 - Coal and Coal Fly Ash.

Analytical Results (μg/g): Coal Samples

| | SRM 1632 Coal | | SRM 1633 Coal Fly Ash | |
|---|---|---|---|---|
| element | NBS value | this work | NBS value | this work |
| Al % | 1.78 | 1.66 ± 0.12 | 12.5 | 11.5 ± 0.8 |
| As | 5.9 ± 0.6 | 6.1 ± 0.4 | 61 ± 6 | 65 ± 4 |
| Ba | 342 | 338 ± 8 | 2690 | 2735 ± 165 |
| Ca % | 0.41 | 0.43 ± 0.02 | 4.60 | 4.8 ± 0.4 |
| Cr | 20.2 ± 0.5 | - | 131 ± 2 | 119 ± 2 |
| Cu | 18 ± 2 | 14 ± 0.5 | 128 ± 5 | 128 ± 11 |
| Fe % | 0.87 | 0.85 ± 0.01 | 6.18 | 5.9 ± 0.3 |
| K % | 0.29 | 0.27 ± 0.02 | 1.68 | 1.6 ± 0.2 |
| Mg % | 0.16 | 0.14 ± 0.02 | 1.55 | 1.48 ± 0.1 |
| Mn | 40 ± 3 | 39 ± 2 | 493 ± 7 | 500 ± 21 |
| Na % | 0.038 | 0.039 ± 0.006 | 0.32 | 0.32 ± 0.01 |
| P | 71 | 73 ± 4 | 880 | 883 ± 32 |
| Pb | 21.1 | 18.9 ± 0.8 | 70 ± 4 | 64 ± 6 |
| S % | 1.35 | 0.037 ± 0.006 | 0.50 | 0.07 ± 0.001 |
| Sb | 3.56 | 3.42 ± 0.18 | 6.9 | 6.8 ± 0.3 |
| Si % | 3.38 | 3.42 ± 0.10 | 20.5 | 21.8 ± 2.7 |
| Sn | 10.1 | 10.2 ± 0.5 | 10.9 | 10.8 ± 1.0 |
| Sr | 153 | 151 ± 5 | 1410 | 1425 ± 44 |
| Ti % | 0.093 | 0.106 ± 0.003 | 0.72 | 0.76 ± 0.02 |
| V | 35 ± 3 | 37 ± 3 | 214 ± 8 | 208 ± 8 |
| Zn | 37 ± 4 | 35 ± 2 | 210 ± 20 | 213 ± 8 |
| Zr | 45 | 25 ± 4 | 303 | 208 ± 3 |

standard was chosen and run as an 'unknown' to verify the results (42).

A comparison between ashing vessels - porcelain versus Vycor - carried out under similar ashing conditions and dissolution techniques is seen in Tables XI and XII. Elemental analysis data obtained using porcelain and Vycor crucibles for the NBS SRM 1571 Orchard Leaves are compared in Table XI, while a similar set of data for NBS SRM 1570 Spinach is compared in Table XII. Orchard leaves were ashed with newly prepared Vycor crucibles.

Discrepancies occurred for Al, Cr, Cu, Fe, Na, Ni and Pb. Lead is often lost during the ashing step if the temperature of the furnace rises too high (60). Low recoveries are often observed for Al, Cr, Cu, Fe and Ni (60,61,63,71). This may be the result of incomplete dissolution or extraction of these elements from the dry ashed product and/or the result of occlusion by the insoluble silica residue. Excessive Na in the porcelain crucibles could be due to poor cleaning of the crucible prior to use. Difficulties were encountered with several trace elements - Cd, Cr and Ni - because they are at or near the detection limit of the ICP.

No major difference was noted in either set of data. Both types of vessels seem to give results comparable to the NBS values. However, with the NBS SRM 1570 Spinach sample it was noted that the relative standard deviation is much lower for the vycor crucibles on second usage as they were first used to analyze the NBS SRM 1571 Orchard Leaves. This

Table XI. Comparison of Crucible Materials in the Sample Preparation of NBS SRM 1571 Orchard Leaves.

| Sample Preparation using NBS SRM 1571 ORCHARD LEAVES | | | | | |
|---|---|---|---|---|---|
| ELEMENT | NBS value | ASH#1* $\bar{X}$, s | RSD | ASH#2* $\bar{X}$, s | RSD |
| Al | - | 404.01 / 62.32 | 15.3% | 260.29 / 24.41 | 9.38% |
| B | 33 ± 3 | 32.79 / 0.50 | 1.52% | 31.93 / 1.18 | 3.68% |
| Ca% | 2.09 ± 0.03 | 2.05 / 0.01 | 0.65% | 1.97 / 0.07 | 3.52% |
| Cr | 2.6 ± 0.3 | 2.11 / 0.09 | 4.41% | 2.35 / 0.15 | 6.41% |
| Cu | 12 ± 1 | 16.04 / 1.89 | 11.8% | 10.20 / 0.74 | 7.26% |
| Fe | 300 ± 20 | 264.85 / 18.04 | 6.81% | 231.85 / 27.46 | 11.85% |
| K% | 1.47 ± 0.03 | 0.91 / 0.16 | 17.1% | 1.19 / 0.17 | 14.38% |
| Mg% | 0.62 ± 0.02 | 0.58 / 0.006 | 1.01% | 0.57 / 0.02 | 3.11% |
| Mn | 91 ± 4 | 84.59 / 2.15 | 2.54% | 82.26 / 3.13 | 3.81% |
| Na | 82 ± 6 | 725.10 / 165.74 | 22.8% | 73.68 / 15.84 | 21.15% |
| Ni | 1.3 ± 0.2 | 1.33 / 0.06 | 4.92% | 0.95 / 0.11 | 11.29% |
| P% | 0.21 ± 0.01 | 0.20 / 0.002 | 0.82% | 0.20 / 0.01 | 4.34% |
| Pb | 45 ± 3 | 31.83 / 2.21 | 6.94% | 12.93 / 6.70 | 51.83% |
| Zn | 25 ± 3 | 24.27 / 1.72 | 7.09% | 22.96 / 3.97 | 17.29% |

* ASH #1 : Porcelain Crucible Dry Ash (485°C for 18 hours)
ASH #2 : Vycor Crucible Dry Ash (485°C for 18 hours)

Table XII. Comparison of Crucible Materials in the Sample Preparation of NBS SRM 1570 Spinach.

| Sample Preparation using NBS SRM 1570 SPINACH | | | | | |
|---|---|---|---|---|---|
| ELEMENT | NBS value | ASH#1* $\bar{X}$, s | RSD | ASH#2* X, s | RSD |
| Al | 870 ± 50 | 1085 / 225 | 20.8 % | 740.62 / 38.21 | 5.16% |
| B | (30) | 27.86 / 0.73 | 2.64% | 27.30 / 0.39 | 1.42% |
| Ca% | 1.35 ± 0.03 | 1.24 / 0.03 | 2.70% | 1.28 / 0.04 | 2.90% |
| Cr | 4.6 ± 0.3 | 3.86 / 0.42 | 10.9 % | 3.74 / 0.50 | 13.4% |
| Cu | 12 ± 2 | 17.52 / 4.22 | 24.1 % | 11.21 / 0.14 | 1.21% |
| Fe | 550 ± 20 | 512.31 / 31.55 | 6.16 % | 507.65 / 9.11 | 1.79 % |
| K% | 3.56 ± 0.03 | 2.64 / 0.38 | 14.3 % | 3.34 / 0.07 | 2.00 % |
| Mg% | – | 0.83 / 0.01 | 1.52% | 0.84 / 0.005 | 0.60% |
| Mn | 165 ± 6 | 155.27 / 4.85 | 3.12% | 157.62 / 2.20 | 1.39% |
| Na% | – | 1.41 / 0.06 | 3.96% | > | - % |
| Ni | (6) | 5.44 / 0.30 | 5.51% | 5.39 / 0.35 | 6.54% |
| P% | 0.55 ± 0.02 | 0.54 / 0.007 | 1.29% | 0.53 / 0.007 | 1.26% |
| Pb | 1.2 ± 0.2 | 3.68 / 0.93 | 25.29% | 3.43 / 0.54 | 15.83% |
| Zn | 50 ± 2 | 45.37 / 6.74 | 14.86% | 42.27 / 2.37 | 5.60% |

* ASH # 1 : Porcelain Crucible Dry Ash (485°C for 18 hours)
ASH # 2 : Vycor Crucible Dry Ash (485°C for 18 hours)

may be due to contaminants being removed with the first heating in the muffle furnace of the orchard leaf samples. Each sample was analyzed in triplicate for three sample weights. Lower sample weights allowed the major elements to be determined more accurately as higher sample weights caused overranging for some of the major components in plant tissues. This comparison indicates that either type of crucible is suitable for analysis without excessive errors being incurred.

Data collected for the three NBS standards selected for analysis are shown on the next few pages. Each standard was analyzed at sample weights of 1.00, 0.50 and 0.25 grams. These weights were chosen to enable determination of the major matrix elements (K, P, Ca, Mg and Fe) which often saturate the readout electronics of the PMT's.

Each sample weight was made up in triplicate to give nine samples for analysis and each of the nine were analyzed in triplicate to give the data tables containing twenty-seven runs per element per standard. This was done to obtain relative standard deviations (RSD) in precision studies. The tables containing actual data obtained have all been corrected for dilution. Thus the mean is the concentration value which can be used to compare with certified values.

Data summaries tabulated in Tables XIII, XV and XVII contain actual raw data that have been corrected for dilution, means, and standard deviations for the NBS Standards - Orchard Leaves, Spinach and Tomato Leaves. Overall summaries

Table XIII. Raw Data for NBS SRM 1571 Orchard Leaves(μg/g).

Runs 1 through 9 weigh approximately 1.00 gram.
Runs 10 through 18 weigh approximately 0.50 grams.
Runs 19 through 27 weigh approximately 0.25 grams.
The Ca values in runs 1 through 9 are not valid as saturation of the PMT occurred. Runs 10 through 27 did not cause overranging and they were used to obtain the value shown in Table XIV.
The Ni values in runs 10 through 27 are too low for detection. Only runs 1 through 9, one-gram samples, gave a detectable level for Ni and were used for determining the value shown in Table XIV.

NBS SRM 1571 ORCHARD LEAVES

DATA SUMMARY

| RUN | AL | B | CA | CD1 | CD2 | CR | CU |
|---|---|---|---|---|---|---|---|
| 1 | 212.6 | 31.28 | 11157.2 | < 0.3497 < | 3.932 | 2.309 | 10.60 |
| 2 | 210.4 | 30.85 | 11156.1 | < 0.3497 < | 3.932 | 2.236 | 10.46 |
| 3 | 213.9 | 31.01 | 11156.1 | < 0.3497 < | 3.932 | 2.232 | 10.61 |
| 4 | 237.2 | 31.47 | 10982.3 | < 0.3442 < | 3.870 | 2.193 | 10.57 |
| 5 | 241.8 | 31.22 | 10981.7 | < 0.3442 < | 3.870 | 2.185 | 10.52 |
| 6 | 249.7 | 31.24 | 10981.7 | < 0.3442 < | 3.870 | 2.218 | 10.57 |
| 7 | 232.3 | 30.50 | 11409.0 | < 0.3577 < | 4.022 | 2.173 | 10.51 |
| 8 | 257.4 | 31.33 | 11410.4 | < 0.3577 < | 4.022 | 2.271 | 10.87 |
| 9 | 245.4 | 30.40 | 11409.5 | < 0.3577 < | 4.022 | 2.181 | 10.66 |
| 10 | 272.1 | 31.86 | 19374.4 | < 0.6720 < | 7.555 | 2.288 | 10.57 |
| 11 | 271.8 | 31.89 | 19417.1 | < 0.6720 < | 7.555 | 2.265 | 10.54 |
| 12 | 272.1 | 31.55 | 19213.5 | < 0.6720 < | 7.555 | 2.214 | 10.43 |
| 13 | 272.4 | 31.76 | 19128.4 | < 0.6954 < | 7.819 | 2.295 | 10.69 |
| 14 | 270.1 | 31.20 | 18921.0 | < 0.6954 < | 7.819 | 2.292 | 10.60 |
| 15 | 298.9 | 32.12 | 19444.7 | < 0.6954 < | 7.819 | 2.381 | 10.90 |
| 16 | 266.2 | 31.65 | 19293.3 | < 0.6947 < | 7.811 | 2.351 | 10.36 |
| 17 | 276.5 | 31.49 | 19242.0 | < 0.6947 < | 7.811 | 2.232 | 10.47 |
| 18 | 274.8 | 31.30 | 19124.7 | < 0.6947 < | 7.811 | 2.290 | 10.41 |
| 19 | 257.4 | 35.2 | 21202.5 | < 1.459 < | 16.40 | 2.69 | 8.40 |
| 20 | 254.2 | 34.7 | 21016.2 | < 1.459 < | 16.40 | 2.51 | 8.33 |
| 21 | 260.9 | 34.7 | 21071.3 | < 1.459 < | 16.40 | 2.50 | 8.54 |
| 22 | 273.4 | 32.6 | 19997.1 | < 1.371 < | 15.41 | 2.467 | 9.49 |
| 23 | 260.0 | 32.5 | 19779.0 | < 1.371 < | 15.41 | 2.543 | 9.62 |
| 24 | 261.0 | 32.0 | 19654.5 | < 1.371 < | 15.41 | 2.374 | 9.27 |
| 25 | 288.5 | 32.2 | 19700.1 | < 1.403 < | 15.77 | 2.54 | 10.49 |
| 26 | 297.5 | 32.1 | 19545.6 | < 1.403 < | 15.77 | 2.61 | 10.39 |
| 27 | 299.5 | 32.0 | 19491.5 | < 1.403 < | 15.77 | 2.57 | 10.45 |
| MEAN | 260.3 | 31.934 | 16861.5 | < 1.459 < | 16.40 | 2.3489 | 10.197 |
| S.D. | 24.4 | 1.177 | 4131.5 | < 1.459 < | 16.40 | 0.1506 | 0.740 |

Table XIII. Continued.

| RUN | FE | K | MG | MN | NA | NI | P |
|---|---|---|---|---|---|---|---|
| 1 | 183.6 | 12133.1 | 5586.2 | 77.71 | 65.52 | 0.9527 | 1955.2 |
| 2 | 183.7 | 13105.4 | 5502.2 | 77.30 | 22.43 | 0.8622 | 1935.9 |
| 3 | 187.8 | 13184.4 | 5523.8 | 78.08 | 71.66 | 1.051 | 1917.0 |
| 4 | 202.3 | 11386.9 | 5578.9 | 79.19 | 66.25 | 0.9079 | 1942.9 |
| 5 | 206.7 | 12498.0 | 5537.1 | 79.04 | 72.46 | 0.9005 | 1935.3 |
| 6 | 219.4 | 14339.4 | 5536.3 | 80.68 | 83.55 | 1.0093 | 1909.5 |
| 7 | 196.8 | 11632.6 | 5423.4 | 76.86 | 69.81 | 0.9256 | 1902.3 |
| 8 | 236.1 | 14193.7 | 5599.7 | 82.10 | 88.50 | 1.059 | 2262.3 |
| 9 | 219.6 | 12703.0 | 5475.7 | 79.24 | 79.46 | 0.9899 | 1921.0 |
| 10 | 245.5 | 11178.8 | 5645.6 | 82.3 | 71.4 < | 1.574 | 1967.7 |
| 11 | 254.1 | 12903.2 | 5665.6 | 83.6 | 81.0 < | 1.574 | 1982.5 |
| 12 | 262.0 | 13146.1 | 5607.4 | 84.1 | 83.0 < | 1.574 | 1945.5 |
| 13 | 237.6 | 11958.0 | 5580.7 | 81.6 | 79.4 < | 1.629 | 1941.8 |
| 14 | 235.8 | 11481.1 | 5525.6 | 80.7 | 76.6 < | 1.629 | 1904.8 |
| 15 | 293.4 | 13966.6 | 5687.5 | 85.0 | 98.4 < | 1.629 | 1954.8 |
| 16 | 231.9 | 10137.6 | 5620.0 | 82.0 | 68.3 < | 1.627 | 1932.3 |
| 17 | 242.7 | 13699.0 | 5606.2 | 83.3 | 91.1 < | 1.627 | 1938.5 |
| 18 | 241.1 | 12653.4 | 5571.8 | 83.1 | 86.6 < | 1.627 | 1916.3 |
| 19 | 221.3 | 7462.1 | 6129.3 | 87.3 | 44.4 < | 3.416 | 2126.6 |
| 20 | 220.9 | 8192.0 | 6075.1 | 86.7 | 49.9 < | 3.416 | 2128.1 |
| 21 | 235.9 | 11252.7 | 6084.5 | 88.6 | 71.7 < | 3.416 | 2110.8 |
| 22 | 244.5 | 12834.5 | 5749.6 | 85.5 | 84.0 < | 3.210 | 1971.6 |
| 23 | 223.9 | 9274.1 | 5657.3 | 80.8 | 63.0 < | 3.210 | 1934.4 |
| 24 | 233.3 | 10456.4 | 5644.7 | 82.2 | 69.8 < | 3.210 | 1915.5 |
| 25 | 255.5 | 10683.6 | 5691.5 | 84.4 | 74.3 < | 3.285 | 1992.7 |
| 26 | 267.7 | 12389.6 | 5646.4 | 84.6 | 86.2 < | 3.285 | 1926.4 |
| 27 | 276.7 | 12767.2 | 5635.2 | 84.8 | 90.6 < | 3.416 | 1949.8 |
| MEAN | 231.8 | 11911.6 | 5651.4 | 82.26 | 73.68 < | 3.416 | 1971.2 |
| S.D. | 27.5 | 1713.4 | 175.5 | 3.13 | 15.84 < | 3.416 | 85.5 |

| RUN | PB | ZN |
|---|---|---|
| 1 | 18.40 | 22.07 |
| 2 | 18.23 | 21.77 |
| 3 | 18.81 | 22.04 |
| 4 | 11.63 | 20.49 |
| 5 | 11.76 | 20.55 |
| 6 | 12.56 | 20.93 |
| 7 | 11.27 | 21.60 |
| 8 | 12.42 | 22.86 |
| 9 | 11.76 | 22.21 |
| 10 | 13.80 | 24.14 |
| 11 | 13.25 | 24.22 |
| 12 | 13.44 | 24.13 |
| 13 | 10.24 | 24.32 |
| 14 | 10.27 | 24.11 |
| 15 | 10.89 | 25.23 |
| 16 | 8.10 | 20.18 |
| 17 | 7.65 | 20.55 |
| 18 | 7.84 | 20.38 |
| 19 | 5.51 | 19.90 |
| 20 | 4.54 | 19.60 |
| 21 | 5.75 | 19.92 |
| 22 | 8.65 | 20.28 |
| 23 | 8.59 | 19.97 |
| 24 | 8.08 | 19.76 |
| 25 | 28.7 | 32.9 |
| 26 | 29.2 | 33.1 |
| 27 | 27.7 | 32.9 |
| MEAN | 12.93 | 22.96 |
| S.D. | 6.70 | 3.97 |

Table XIV. Comparison of NBS Certified Values and Values Found for NBS SRM 1571 Orchard Leaves.

| Analytical Results (μg/g): NBS SRM 1571 ORCHARD LEAVES | | | | |
|---|---|---|---|---|
| Element | Mean | Standard Deviation | RSD | NBS value |
| Al | 260.29 | 24.41 | 9.38% | - |
| B | 31.93 | 1.18 | 3.68% | 33 ± 3 |
| Ca% | 1.97 | 0.07 | 3.52% | 2.09 ± 0.03 |
| Cr | 2.35 | 0.15 | 6.41% | 2.6 ± 0.3 |
| Cu | 10.20 | 0.74 | 7.26% | 12 ± 1 |
| Fe | 231.85 | 27.46 | 11.85% | 300 ± 20 |
| K% | 1.19 | 0.17 | 14.38% | 1.47 ± 0.03 |
| Mg% | 0.57 | 0.02 | 3.11% | 0.62 ± 0.02 |
| Mn | 82.26 | 3.13 | 3.81% | 91 ± 4 |
| Na | 73.68 | 15.84 | 21.15% | 82 ± 6 |
| Ni | 0.95 | 0.11 | 11.29% | 1.3 ± 0.2 |
| P% | 0.20 | 0.008 | 4.34% | 0.21 ± 0.01 |
| Pb | 12.93 | 6.70 | 51.83% | 45 ± 3 |
| Zn | 22.96 | 3.97 | 17.29% | 25 ± 3 |

Table XV. Raw Data for NBS SRM 1570 Spinach (μg/g).

Runs 1 through 9 weigh approximately 0.25 grams.
Runs 10 through 18 weigh approximately 0.50 grams.
Runs 19 through 27 weigh approximately 1.00 gram.
Ca in runs 19 through 27 overranged and are not valid.
Na in all cases actually overranged. The concentration value given is not the true value; it is only a value calculated on the basis of millivolt intensities for that PMT and the calibration coefficient determined by CAL.

NBS SRM 1570 SPINACH

DATA SUMMARY

| RUN | AL | B | CA | | CD1 | | CD2 | CR | CU |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 672.5 | 27.8 | 12704.0 | < | 1.425 | < | 16.02 | 3.36 | 11.17 |
| 2 | 669.4 | 27.5 | 12636.6 | < | 1.425 | < | 16.02 | 3.41 | 11.05 |
| 3 | 671.4 | 27.7 | 12646.8 | < | 1.425 | < | 16.02 | 3.30 | 11.19 |
| 4 | 702.5 | 27.8 | 12217.7 | < | 1.440 | < | 16.19 | 3.30 | 11.20 |
| 5 | 704.0 | 27.5 | 12158.9 | < | 1.440 | < | 16.19 | 3.14 | 11.22 |
| 6 | 696.3 | 27.3 | 12092.8 | < | 1.440 | < | 16.19 | 3.12 | 11.01 |
| 7 | 723.1 | 27.9 | 12881.0 | < | 1.418 | < | 15.94 | 3.10 | 11.23 |
| 8 | 724.0 | 28.0 | 12891.2 | < | 1.418 | < | 15.94 | 3.26 | 11.43 |
| 9 | 719.4 | 27.7 | 12791.6 | < | 1.418 | < | 15.94 | 3.12 | 11.19 |
| 10 | 801.9 | 27.41 | 13277.7 | < | 0.6908 | < | 7.767 | 3.992 | 11.50 |
| 11 | 801.9 | 27.37 | 13281.7 | < | 0.6908 | < | 7.767 | 3.937 | 11.38 |
| 12 | 797.3 | 27.19 | 13198.0 | < | 0.6908 | < | 7.767 | 3.952 | 11.36 |
| 13 | 755.4 | 27.31 | 13130.4 | < | 0.7140 | < | 8.028 | 3.693 | 11.12 |
| 14 | 760.6 | 27.39 | 13206.2 | < | 0.7140 | < | 8.028 | 3.768 | 11.20 |
| 15 | 758.1 | 27.34 | 13145.8 | < | 0.7140 | < | 8.028 | 3.733 | 11.21 |
| 16 | 787.2 | 27.50 | 12967.6 | < | 0.7094 | < | 7.977 | 3.757 | 11.11 |
| 17 | 782.2 | 27.39 | 12873.0 | < | 0.7094 | < | 7.977 | 3.663 | 11.06 |
| 18 | 782.7 | 27.38 | 12842.0 | < | 0.7094 | < | 7.977 | 3.637 | 11.06 |
| 19 | 746.5 | 26.52 | 10050.7 | < | 0.3539 | < | 3.980 | 3.734 | 11.01 |
| 20 | 751.4 | 26.71 | 10051.2 | < | 0.3539 | < | 3.980 | 3.782 | 11.10 |
| 21 | 752.8 | 26.78 | 10051.8 | < | 0.3539 | < | 3.980 | 3.778 | 11.14 |
| 22 | 743.0 | 26.98 | 10145.3 | < | 0.3572 | < | 4.016 | 4.876 | 11.23 |
| 23 | 738.4 | 26.82 | 10144.8 | < | 0.3572 | < | 4.016 | 4.841 | 11.17 |
| 24 | 739.5 | 26.88 | 10144.8 | < | 0.3572 | < | 4.016 | 4.856 | 11.21 |
| 25 | 741.8 | 27.19 | 9987.8 | < | 0.3517 | < | 3.954 | 4.008 | 11.47 |
| 26 | 734.8 | 26.89 | 9986.5 | < | 0.3517 | < | 3.954 | 3.931 | 11.30 |
| 27 | 738.6 | 26.96 | 9987.0 | < | 0.3517 | < | 3.954 | 3.945 | 11.35 |
| MEAN | 740.6 | 27.304 | 11907.1 | < | 1.440 | < | 16.19 | 3.740 | 11.2098 |
| S.D. | 38.2 | 0.387 | 1364.4 | < | 1.440 | < | 16.19 | 0.499 | 0.1355 |

Table XV. Continued.

| RUN | FE | K | MG | MN | NA | NI | P |
|---|---|---|---|---|---|---|---|
| 1 | 494.7 | 32443.1 | 8443.5 | 160.5 | 13349.3 | 5.06 | 5387.6 |
| 2 | 491.8 | 32355.3 | 8404.0 | 159.7 | 13303.3 | 4.73 | 5394.0 |
| 3 | 491.9 | 32342.8 | 8411.7 | 159.6 | 13300.0 | 4.68 | 5356.2 |
| 4 | 501.9 | 32766.9 | 8429.1 | 158.7 | 13571.1 | 5.08 | 5391.7 |
| 5 | 497.5 | 32645.3 | 8394.3 | 158.0 | 13527.3 | 4.97 | 5359.4 |
| 6 | 494.3 | 32579.5 | 8354.1 | 157.1 | 13489.6 | 5.04 | 5272.0 |
| 7 | 517.9 | 32856.0 | 8436.7 | 160.2 | 13569.1 | 4.99 | 5302.9 |
| 8 | 516.3 | 32721.3 | 8432.0 | 160.0 | 13484.6 | 5.45 | 5245.5 |
| 9 | 512.9 | 32676.4 | 8374.7 | 159.1 | 13467.7 | 4.76 | 5280.6 |
| 10 | 519.6 | 33438.9 | 8450.6 | 159.2 | 13597.8 | 5.61 | 5279.5 |
| 11 | 519.1 | 33631.0 | 8441.3 | 158.9 | 13685.5 | 5.42 | 5230.8 |
| 12 | 515.6 | 33414.6 | 8381.1 | 157.8 | 13579.2 | 5.55 | 5193.2 |
| 13 | 512.9 | 33661.1 | 8386.6 | 158.6 | 13617.7 | 5.28 | 5282.9 |
| 14 | 515.0 | 33904.9 | 8424.9 | 159.2 | 13702.8 | 5.40 | 5253.1 |
| 15 | 512.5 | 33837.0 | 8396.2 | 158.5 | 13656.1 | 5.55 | 5207.5 |
| 16 | 518.7 | 33709.3 | 8513.7 | 159.8 | 13691.6 | 5.81 | 5320.5 |
| 17 | 515.0 | 33528.2 | 8456.6 | 158.8 | 13593.4 | 5.61 | 5242.1 |
| 18 | 514.2 | 33505.8 | 8445.5 | 158.4 | 13596.1 | 5.62 | 5198.1 |
| 19 | 501.1 | 33758.3 | 8312.1 | 153.2 | 13457.7 | 5.381 | 5158.4 |
| 20 | 504.4 | 33982.5 | 8372.2 | 154.2 | 13531.3 | 5.509 | 5195.3 |
| 21 | 504.3 | 33976.3 | 8378.5 | 154.2 | 13513.6 | 5.559 | 5169.9 |
| 22 | 513.7 | 34130.2 | 8396.2 | 156.2 | 13552.1 | 5.596 | 5215.6 |
| 23 | 510.3 | 33954.2 | 8337.1 | 155.4 | 13466.9 | 5.564 | 5273.4 |
| 24 | 510.1 | 34048.5 | 8326.7 | 155.3 | 13484.7 | 5.739 | 5156.0 |
| 25 | 504.7 | 34531.1 | 8428.3 | 156.3 | 13617.3 | 5.904 | 5267.8 |
| 26 | 497.3 | 34172.2 | 8301.8 | 154.2 | 13478.0 | 5.794 | 5161.9 |
| 27 | 498.8 | 34395.0 | 8332.4 | 154.7 | 13542.9 | 5.80 | 5155.5 |
| MEAN | 507.65 | 33443.2 | 8398.6 | 157.621 | 13534.3 | 5.387 | 5257.5 |
| S.D. | 9.11 | 668.5 | 50.0 | 2.195 | 105.4 | 0.352 | 75.0 |

| RUN | PB | ZN |
|---|---|---|
| 1 | 3.04 | 45.2 |
| 2 | 2.017 | 44.9 |
| 3 | 2.279 | 45.0 |
| 4 | 3.02 | 44.6 |
| 5 | 2.65 | 44.5 |
| 6 | 2.75 | 44.2 |
| 7 | 3.44 | 46.0 |
| 8 | 4.14 | 46.1 |
| 9 | 3.21 | 45.8 |
| 10 | 3.809 | 41.58 |
| 11 | 3.263 | 41.54 |
| 12 | 3.492 | 41.19 |
| 13 | 3.189 | 42.20 |
| 14 | 3.215 | 42.43 |
| 15 | 3.583 | 42.28 |
| 16 | 3.951 | 42.63 |
| 17 | 3.377 | 42.31 |
| 18 | 3.638 | 42.28 |
| 19 | 3.572 | 39.85 |
| 20 | 3.747 | 40.13 |
| 21 | 3.747 | 40.24 |
| 22 | 3.933 | 38.92 |
| 23 | 3.775 | 38.75 |
| 24 | 4.254 | 38.91 |
| 25 | 3.943 | 40.22 |
| 26 | 3.743 | 39.73 |
| 27 | 3.77 | 39.9 |
| MEAN | 3.43 | 42.3 |
| S.D. | 0.543 | 2.368 |

Table XVI. Comparison of NBS Certified Values and Values Found for NBS SRM 1570 Spinach.

| Analytical Results (μg/g): NBS SRM 1570 SPINACH | | | | |
|---|---|---|---|---|
| Element | Mean | Standard Deviation | RSD | NBS value |
| Al | 740.62 | 38.21 | 5.16% | 870 ± 50 |
| B | 27.30 | 0.39 | 1.42% | (30) |
| Ca % | 1.28 | 0.04 | 2.90% | 1.35 ± 0.03 |
| Cr | 3.74 | 0.50 | 13.35% | 4.6 ± 0.3 |
| Cu | 11.21 | 0.14 | 1.21% | 12 ± 2 |
| Fe | 507.65 | 9.11 | 1.79% | 550 ± 20 |
| K % | 3.34 | 0.07 | 2.00% | 3.56 ± 0.03 |
| Mg % | 0.84 | 0.005 | 0.60% | - |
| Mn | 157.62 | 2.20 | 1.39% | 165 ± 6 |
| Na % | > | - | - | - |
| Ni | 5.39 | 0.35 | 6.54% | (6) |
| P % | 0.53 | 0.007 | 1.26% | 0.55 ± 0.02 |
| Pb | 3.43 | 0.54 | 15.83% | 1.2 ± 0.2 |
| Zn | 42.27 | 2.37 | 5.60% | 50 ± 2 |

Table XVII. Raw Data for NBS SRM 1573 Tomato Leaves (μg/g).

Runs 1 through 9 weigh approximately 0.25 grams.
Runs 10 through 18 weigh approximately 0.50 grams.
Runs 19 through 27 weigh approximately 1.00 gram.
Ca overranged for runs 19 through 27 and thus do not represent a true value for Ca.
Ni was too low to be detected at sample weights less than 1.00 gram.
Pb values were extremely erratic at a sample weight of 0.25 grams. Therefore they were not used in calculating the Pb value shown Table XVIII.

NBS TOMATO LEAVES

DATA SUMMARY

| RUN | AL | B | CA | | CD1 | | CD2 | CR | CU |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 685.9 | 37.1 | 29431.3 | < | 1.372 | < | 15.42 | 3.76 | 9.31 |
| 2 | 678.8 | 37.0 | 29210.7 | < | 1.372 | < | 15.42 | 3.63 | 9.22 |
| 3 | 678.8 | 36.8 | 29201.4 | < | 1.372 | < | 15.42 | 3.59 | 9.12 |
| 4 | 736.6 | 36.7 | 29017.9 | < | 1.408 | < | 15.83 | 3.30 | 9.30 |
| 5 | 731.9 | 36.8 | 28935.8 | < | 1.408 | < | 15.83 | 3.33 | 9.28 |
| 6 | 730.4 | 36.6 | 28814.4 | < | 1.408 | < | 15.83 | 3.38 | 9.15 |
| 7 | 727.4 | 36.6 | 29082.1 | < | 1.378 | < | 15.49 | 3.50 | 9.43 |
| 8 | 720.8 | 36.5 | 28956.7 | < | 1.378 | < | 15.49 | 3.49 | 9.29 |
| 9 | 721.1 | 36.5 | 28968.0 | < | 1.378 | < | 15.49 | 3.50 | 9.30 |
| 10 | 760.4 | 36.63 | 18759.4 | < | 0.6965 | < | 7.831 | 3.567 | 9.62 |
| 11 | 750.0 | 36.06 | 18757.9 | < | 0.6965 | < | 7.831 | 3.384 | 9.53 |
| 12 | 753.6 | 36.23 | 18758.9 | < | 0.6965 | < | 7.831 | 3.452 | 9.52 |
| 13 | 774.1 | 36.77 | 19045.7 | < | 0.7072 | < | 7.951 | 3.601 | 9.97 |
| 14 | 770.8 | 36.31 | 19045.7 | < | 0.7072 | < | 7.951 | 3.553 | 9.95 |
| 15 | 770.8 | 36.26 | 19045.2 | < | 0.7072 | < | 7.951 | 3.463 | 9.95 |
| 16 | 785.6 | 36.40 | 19096.1 | < | 0.7090 | < | 7.972 | 3.470 | 9.74 |
| 17 | 783.8 | 36.38 | 19097.0 | < | 0.7090 | < | 7.972 | 3.504 | 9.77 |
| 18 | 778.7 | 36.11 | 19095.6 | < | 0.7090 | < | 7.972 | 3.520 | 9.74 |
| 19 | 790.5 | 35.51 | 9531.9 | < | 0.3528 | < | 3.967 | 3.589 | 10.13 |
| 20 | 798.2 | 35.93 | 9532.4 | < | 0.3528 | < | 3.967 | 3.655 | 10.26 |
| 21 | 758.7 | 34.11 | 9531.0 | < | 0.3528 | < | 3.967 | 3.464 | 9.818 |
| 22 | 734.2 | 34.69 | 9491.6 | < | 0.3513 | < | 3.950 | 3.567 | 9.748 |
| 23 | 741.2 | 35.11 | 9491.4 | < | 0.3513 | < | 3.950 | 3.591 | 9.853 |
| 24 | 740.8 | 35.06 | 9491.4 | < | 0.3513 | < | 3.950 | 3.576 | 9.861 |
| 25 | 757.9 | 35.79 | 9587.7 | < | 0.3549 | < | 3.990 | 3.660 | 10.14 |
| 26 | 759.6 | 35.91 | 9588.2 | < | 0.3549 | < | 3.990 | 3.698 | 10.16 |
| 27 | 750.7 | 35.53 | 9587.9 | < | 0.3549 | < | 3.990 | 3.714 | 10.17 |
| MEAN | 747.1 | 36.125 | 19191.6 | < | 1.408 | < | 15.83 | 3.5376 | 9.680 |
| S.D. | 31.9 | 0.726 | 8129.3 | < | 1.408 | < | 15.83 | 0.1143 | 0.352 |

Table XVII. Continued.

| RUN | FE | K | MG | MN | NA | NI | P |
|---|---|---|---|---|---|---|---|
| 1 | 522.2 | 39264.7 | 6563.2 | 219.9 | 545.1 < | 3.213 | 3398.1 |
| 2 | 518.4 | 39057.8 | 6508.9 | 218.2 | 543.2 < | 3.213 | 3425.2 |
| 3 | 519.0 | 39085.1 | 6505.1 | 217.9 | 542.8 < | 3.213 | 3425.8 |
| 4 | 547.7 | 39017.8 | 6486.6 | 217.9 | 575.1 < | 3.298 | 3382.9 |
| 5 | 546.5 | 38926.8 | 6466.8 | 217.3 | 573.6 < | 3.298 | 3358.6 |
| 6 | 544.0 | 38768.1 | 6434.2 | 216.3 | 570.8 < | 3.298 | 3324.7 |
| 7 | 533.9 | 37897.0 | 6466.1 | 217.9 | 547.8 < | 3.228 | 3400.2 |
| 8 | 530.8 | 37789.7 | 6433.8 | 217.0 | 545.8 < | 3.228 | 3371.2 |
| 9 | 530.4 | 37798.8 | 6435.0 | 216.9 | 545.9 < | 3.228 | 3333.8 |
| 10 | 555.3 | 40531.4 | 6438.0 | 213.9 | 544.2 < | 1.631 | 3334.1 |
| 11 | 547.2 | 40069.7 | 6346.0 | 210.9 | 538.0 < | 1.631 | 3349.1 |
| 12 | 549.4 | 40300.5 | 6366.8 | 211.5 | 539.8 < | 1.631 | 3356.6 |
| 13 | 562.8 | 41539.8 | 6411.7 | 213.5 | 568.3 < | 1.656 | 3315.2 |
| 14 | 560.0 | 41340.6 | 6378.6 | 212.5 | 565.4 < | 1.656 | 3330.4 |
| 15 | 560.2 | 41364.0 | 6378.6 | 212.4 | 565.3 < | 1.656 | 3320.0 |
| 16 | 577.0 | 41224.7 | 6425.4 | 212.0 | 602.1 < | 1.661 | 3348.2 |
| 17 | 577.4 | 41271.7 | 6432.9 | 212.3 | 602.9 < | 1.661 | 3306.1 |
| 18 | 573.9 | 40930.9 | 6386.1 | 210.8 | 597.3 < | 1.661 | 3287.8 |
| 19 | 554.9 | 41583.0 | 6315.4 | 206.7 | 546.2 | 1.561 | 3254.6 |
| 20 | 560.8 | 41945.5 | 6386.8 | 208.9 | 550.6 | 1.687 | 3284.9 |
| 21 | 534.2 | 39805.5 | 6075.7 | 198.8 | 522.6 | 1.638 | 3163.6 |
| 22 | 534.2 | 40759.8 | 6220.4 | 203.6 | 525.7 | 1.595 | 3236.8 |
| 23 | 539.3 | 41144.0 | 6284.0 | 205.6 | 530.5 | 1.669 | 3285.3 |
| 24 | 538.7 | 41149.9 | 6281.0 | 205.5 | 530.2 | 1.638 | 3305.8 |
| 25 | 547.9 | 42171.1 | 6394.3 | 210.0 | 539.9 | 1.776 | 3340.0 |
| 26 | 550.3 | 42318.1 | 6419.3 | 211.0 | 541.5 | 1.821 | 3366.7 |
| 27 | 542.7 | 41618.3 | 6341.4 | 208.3 | 533.2 < | 3.298 | 3280.4 |
| MEAN | 546.64 | 40321.3 | 6391.9 | 212.13 | 553.10 < | 3.298 | 3329.1 |
| S.D. | 16.27 | 1385.4 | 98.5 | 5.16 | 22.32 < | 3.298 | 58.1 |

| RUN | PB | ZN |
|---|---|---|
| 1 | 2.93 | 56.9 |
| 2 | 1.930 | 56.6 |
| 3 | < 1.922 | 56.5 |
| 4 | 2.299 | 54.5 |
| 5 | 3.01 | 54.3 |
| 6 | 2.57 | 54.1 |
| 7 | 2.107 | 57.7 |
| 8 | 2.61 | 57.5 |
| 9 | 2.394 | 57.5 |
| 10 | 4.609 | 51.3 |
| 11 | 4.113 | 50.55 |
| 12 | 4.440 | 50.71 |
| 13 | 4.103 | 50.00 |
| 14 | 4.213 | 49.83 |
| 15 | 4.017 | 49.76 |
| 16 | 3.658 | 51.8 |
| 17 | 4.015 | 51.8 |
| 18 | 3.806 | 51.5 |
| 19 | 4.217 | 51.39 |
| 20 | 4.450 | 51.98 |
| 21 | 4.241 | 49.42 |
| 22 | 4.663 | 49.29 |
| 23 | 4.785 | 49.84 |
| 24 | 4.748 | 49.92 |
| 25 | 5.185 | 51.62 |
| 26 | 5.240 | 51.84 |
| 27 | 5.70 | 51.3 |
| MEAN | 3.77 | 52.6 |
| S.D. | 1.099 | 2.83 |

Table XVIII. Comparison of NBS Certified Values and Values Found for NBS SRM 1573 Tomato Leaves.

| Analytical Results (μg/g): NBS SRM 1573 TOMATO LEAVES | | | | |
|---|---|---|---|---|
| Element | Mean | Standard Deviation | RSD | NBS value |
| Al | 747.09 | 31.92 | 4.27% | (1200) |
| B | 36.12 | 0.73 | 2.01% | (30) |
| Ca% | 2.91 | 0.02 | 0.63% | 3.00 ± 0.03 |
| Cr | 3.54 | 0.11 | 3.23% | 4.5 ± 0.5 |
| Cu | 9.68 | 0.35 | 3.63% | 11 ± 1 |
| Fe | 546.64 | 16.27 | 2.98% | 690 ± 25 |
| K% | 4.03 | 0.14 | 3.44% | 4.46 ± 0.03 |
| Mg% | 0.64 | 0.008 | 1.20% | (0.70) |
| Mn | 212.64 | 4.51 | 2.12% | 238 ± 7 |
| Na | 554.28 | 21.89 | 3.95% | – |
| Ni | 1.41 | 0.33 | 23.66% | – |
| P% | 0.33 | 0.005 | 1.46% | 0.34 ± 0.02 |
| Pb | 4.46 | 0.53 | 11.94% | 6.3 ± 0.3 |
| Zn | 52.57 | 2.83 | 5.39% | 62 ± 6 |

displaying each element with its mean, standard deviation, relative standard deviation and the certified NBS value, where available for the above mentioned NBS standards are presented in Tables XIV, XVI and XVIII.

For orchard leaves (Table XIII) the one-gram sample weight is represented in runs 1 through 9, sample weights of 0.50 grams are in runs 10 through 18, and the 0.25 gram sample weights are in runs 19 through 27. Spinach and tomato leaves are in reverse order, that is, for Tables XV and XVII the 0.25 gram sample weight is represented in the first nine runs, while one-gram sample weights are represented in the last nine runs, runs 19 through 27. The 0.50 gram sample weight is represented in the same run numbers as orchard leaves.

In any of these samples the Ca content between tables, for example Tables XIII and XIV for orchard leaves, is different because at a sample weight of one gram the readout electronics of the calcium PMT always saturated and thus gave an erroneous value. The lower sample weights gave readings which could be read by the electronics without saturation, after which a dilution correction was applied to give the results shown in Tables XIII, XV and XVII.

Sodium similarly saturated the readout electronics with each sample weight for the spinach samples and thus no value for Na is given in Table XVI. Nickel in the orchard leaf sample was too low to be detectable at weights lower than one-gram. Thus the values for Ni disagree between Tables

XIII and XIV.

In every case for lead analysis, no comparable value to certified values was obtainable. Even precision results were poor with lead. This is because lead requires separation and preconcentration prior to analysis in order to obtain accurate and reproducible results.

An overall summary of the results collected for the three NBS standards and comparison values obtained in this work to those under certification are listed in Table XIX. On the whole, the numbers agree very well.

A more extensive comparison both to certified values and values obtained by other authors for these samples is illustrated in Tables XX, XXI and XXII for orchard leaves, spinach and tomato leaves. In each case an inductively coupled plasma was used in the analysis employing a variety of dissolution techniques. The references pertinent to these three tables are given in Table XXIII and a brief summary of the methods of sample dissolution is presented in Table XXIV. Since orchard leaves has been the oldest NBS botanical standard studied, a wider selection of sample preparation methods can be found in the literature. This is illustrated in Table XX. Many authors, using various dissolution techniques, have difficulty obtaining a value close to the NBS certified value for certain elements. For instance, Al in tomato leaves is quoted as having a value of 1200 ppm (NBS's uncertified value). There is not a single case where a value even approaching this value was found. The value found in this work, 747 ppm,

Table XIX. Overall Summary of NBS Botanicals Comparing Values Found to NBS Values (μg/g).

| ICP ANALYSIS OF NBS SRM's | | | | | | |
|---|---|---|---|---|---|---|
| ORCHARD LEAVES 1571<br>SPINACH 1570<br>TOMATO LEAVES 1573 | | | | | | |
| | 1571 | | 1570 | | 1573 | |
| Element | NBS | this work | NBS | this work | NBS | this work |
| Al | – | 260 ± 24 | 870 ± 50 | 741 ± 38 | (1200) | 747 ± 32 |
| B | 33 ± 3 | 32 ± 1 | (30) | 27 ± 0.5 | (30) | 36 ± 1 |
| Ca% | 2.09 ± 0.03 | 1.97 ± 0.07 | 1.35 ± 0.03 | 1.28 ± 0.04 | 3.00 ± 0.03 | 2.91 ± 0.02 |
| Cr | 2.6 ± 0.3 | 2.4 ± 0.2 | 4.6 ± 0.3 | 3.7 ± 0.5 | 4.5 ± 0.5 | 3.5 ± 0.1 |
| Cu | 12 ± 1 | 10.2 ± 0.7 | 12 ± 2 | 11.2 ± 0.1 | 11 ± 1 | 9.7 ± 0.4 |
| Fe | 300 ± 20 | 232 ± 27 | 550 ± 20 | 508 ± 9 | 690 ± 25 | 547 ± 16 |
| K% | 1.47 ± 0.03 | 1.19 ± 0.17 | 3.56 ± 0.03 | 3.34 ± 0.01 | 4.46 ± 0.03 | 4.03 ± 0.14 |
| Mg% | 0.62 ± 0.02 | 0.57 ± 0.02 | – | 0.84 ± 0.005 | (0.70) | 0.64 ± 0.008 |
| Mn | 91 ± 4 | 82 ± 3 | 165 ± 6 | 158 ± 2.2 | 238 ± 7 | 213 ± 5 |
| Na | 82 ± 6 | 74 ± 16 | – | > | – | 554 ± 22 |
| Ni | 1.3 ± 0.2 | 0.95 ± 0.11 | (6) | 5.4 ± 0.4 | – | 1.4 ± 0.3 |
| P% | 0.21 ± 0.01 | 0.20 ± 0.008 | 0.55 ± 0.02 | 0.53 ± 0.001 | 0.34 ± 0.02 | 0.33 ± 0.005 |
| Pb | 45 ± 3 | 13 ± 7 | 1.2 ± 0.2 | 3.4 ± 0.5 | 6.3 ± 0.3 | 4.5 ± 0.5 |
| Zn | 25 ± 3 | 23 ± 4 | 50 ± 2 | 42 ± 2 | 62 ± 6 | 53 ± 3 |

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Table XX. Literature Survey of Values Found for NBS SRM 1571 Orchard Leaves (µg/g).

NBS SRM 1571 ORCHARD LEAVES

| ELEMENT | NBS | FOUND | a | b | $c_1$ | $c_2$ | $c_3$ | $c_4$ | $c_5$ | $c_6$ | $c_7$ | $c_8$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | - | 260±24 | 377±21 | - | - | - | 227±62 | - | 271 | 301 | 115 | 133 |
| B | 33±3 | 32±1 | - | - | - | - | - | - | - | - | - | - |
| Ca% | 2.09±0.03 | 1.97±0.07 | 1.98±0.07 | 1.98±0.05 | 2.03±0.09 | 2.09±0.03 | 2.04±0.03 | 2.03±0.01 | 2.05 | 1.91 | 1.94 | 2.14 |
| Cr | 2.6±0.3 | 2.4±0.2 | 2 | 2 | - | - | 1.8±0.4 | - | 2.20 | 2.10 | 0.64 | 1.14 |
| Cu | 12±1 | 10±1 | 12±1 | 11±1 | 13±0.2 | 12.3±0.3 | 12.6±0.6 | 13.3±0.12 | 11.9 | 11.7 | 13.8 | 13.1 |
| Fe | 300±20 | 232±29 | 273±4 | 267±6 | 267±5 | 269±23 | 251±25 | 265±1.5 | 248 | 236 | 161 | 299 |
| K% | 1.47±0.03 | 1.26±0.17 | - | - | - | - | 1.49±0.71 | - | 1.44 | 1.45 | 1.76 | 1.48 |
| Mg% | 0.62±0.02 | 0.57±0.02 | 0.57±0.01 | 0.57±0.01 | 0.62±0.00 | 0.58±0.01 | 0.61±0.03 | 0.62±0.00 | 6490 | 5690 | 5930 | 0.67 |
| Mn | 91±4 | 82±3 | 86±2 | 86±1 | 83.3±1.3 | 88.0±1.6 | 86.0±5.6 | 85.5±0.51 | 94.6 | 87.8 | 91.4 | 97.9 |
| Mo | 0.3±6 | 74±16 | - | - | - | - | - | - | - | - | - | - |
| Ni | 1.3±0.2 | 1.0±0.1 | - | - | - | - | 1.4±0.5 | - | 1.74 | 1.20 | 0.927 | 1.11 |
| P% | 0.21±0.01 | 0.20±0.01 | 0.19±0.01 | 0.19±0.00 | - | - | 0.19±0.01 | - | 1800 | 1760 | 1800 | 0.20 |
| Pb | 45±3 | 13±7 | 42±3 | 42±1 | 41±3 | 42±2 | 42.9±1.5 | 44.7±2.3 | 42.9 | 37.1 | 45.4 | 49.1 |
| Zn | 25±3 | 23±4 | 26±1 | 26±1 | 27.7±4.4 | 24.8±0.9 | 26.0±2.7 | 30.0±0.36 | 25.9 | 23.2 | 22.9 | 30.7 |

| ELEMENT | g | h | $i_1$ | $i_2$ | $i_3$ | $i_4$ | $j_1$ | $j_2$ | $j_3$ | $j_4$ | k |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | 234±79 | - | - | - | - | - | 139±43 | 291±19 | 97±33 | 129±43 | - |
| B | 41±7 | - | - | - | - | - | 36±3 | 31±1 | 32±2 | 36±2 | 36±2 |
| Ca% | 1.99±0.07 | 2.00±0.03 | 2.01±0.03 | 2.06±0.02 | 1.99±0.07 | 2.06±0.02 | 1.99±0.05 | 1.97±0.09 | 1.99±0.03 | 1.99±0.05 | 2.28±0.02 |
| Cr | 2.96±0.73 | - | - | - | - | - | 2.4±0.5 | 2.4±0.3 | 2.4±0.5 | 2.4±0.5 | 3.67±0.01 |
| Cu | 17±4 | 12.3±0.72 | 10.8±0.4 | 10.8±0.5 | 17±4 | 10.8±0.5 | 12.4±1.4 | 15±1 | 11±1 | 12±1 | 13.3±0.1 |
| Fe | 183±12 | 269±9.9 | 264±5.6 | 290±3.4 | 183±12 | 290±3.4 | 272±19 | 253±12 | 236±16 | 236±14 | 263±5 |
| K% | 1.66±0.07 | 1.52±0.07 | 1.49±0.05 | 1.44±0.09 | 1.69±0.07 | 1.44±0.09 | 1.42±0.04 | 1.47±0.05 | 1.54±0.05 | 1.44±0.07 | 1.78±0.07 |
| Mg% | 0.62±0.02 | 0.59±0.02 | 0.59±0.01 | 0.61±0.01 | 0.62±0.02 | 0.61±0.01 | 0.62±0.02 | 0.66±0.01 | 0.62±0.03 | 0.62±0.02 | 0.67±0.01 |
| Mn | 101±2 | 88.6±1.3 | 87±1.7 | 90±1.7 | 101±2 | 90±1.7 | 90±3 | 82±5 | 89±2 | 90±3 | 99±0.6 |
| Mo | 140±30 | - | 69±10 | 79±10 | 140±30 | 79±10 | 85±12 | - | 99±15 | 84±10 | - |
| Ni | - | - | - | - | - | - | 1.3±0.4 | 1.5±0.5 | 1.4±0.7 | 1.5±0.5 | 2.1±0.02 |
| P% | 0.22±0.00 | - | 0.19±0.01 | 0.21±0.01 | 0.20±0.00 | 0.21±0.01 | 0.07±.01 | 0.21±0.01 | 0.21±0.01 | 0.02±0.01 | 0.21±0.00 |
| Pb | 48±5 | - | - | - | - | - | 42±3 | 47±2 | 44±3 | 43±3 | 41±1 |
| Zn | 30±5 | 25.1±2.5 | 24.0±1.0 | 26.5±1.3 | 30±5 | 26.5±1.3 | 24.4±1.1 | 25±1 | 25±1 | 25±1 | 19±4 |

Table XXI. Literature Survey of Values Found for NBS SRM 1570 Spinach (µg/g).

| NBS SRM 1570 SPINACH | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ELEMENT | NBS | FOUND | e | f | $i_1$ | $i_2$ | $j_1$ | $j_2$ | $j_3$ | $j_4$ | k |
| Al | 870±50 | 741±38 | - | - | - | - | 818±165 | 638±110 | 779±28 | 840±95 | - |
| B | (30) | 27.3±0.4 | - | 27.8±0.1 | - | - | 28±2 | 27±1 | 27±1 | 27±2 | 20.9±0.3 |
| Ca% | 1.35±0.03 | 1.28±0.04 | - | 1.33±0.02 | 1.33±0.03 | 1.37±0.02 | 1.34±0.02 | 1.36±0.06 | 1.32±0.02 | 1.35±0.03 | 1.54±0.01 |
| Cr | 4.6±0.3 | 3.7±0.5 | - | 1.63±0.04 | - | - | 4.2±0.7 | 2.2±0.2 | 2.7±0.4 | 4.0±0.4 | 6.2±0.1 |
| Cu | 12±2 | 11.2±0.1 | 11.8±2.5 | 11.2±0.01 | 10.9±0.4 | 10.3±0.5 | 12.3±0.8 | 12.5±0.3 | 12.8±0.3 | 12.1±0.4 | 12.1±0.2 |
| Fe | 550±20 | 508±9 | 540±18 | 315±4 | 508±5.6 | 510±3.4 | 533±19 | 537±10 | 515±10 | 525±20 | 511±7 |
| K% | 3.56±0.03 | 3.34±0.07 | - | 3.42±0.01 | 3.47±0.05 | 3.52±0.09 | 3.41±0.24 | 3.45±0.07 | 3.43±0.03 | 3.60±0.09 | 3.29±0.18 |
| Mg% | - | 0.84±0.00 | - | 0.89±0.03 | 0.88±0.01 | 0.92±0.01 | 0.91±0.03 | 0.90±0.02 | 0.90±0.01 | 0.90±0.04 | 0.87±0.01 |
| Mn | 165±6 | 158±2 | 168±3 | 169±0.2 | 160±1.7 | 166±1.7 | 167±4 | 150±4 | 168±12 | 168±6 | 166±1 |
| Na% | - | > | - | 1.33±0.00 | 1.43±0.01 | 1.46±0.01 | 1.33±0.05 | 1.46±0.22 | 1.30±0.08 | 1.30±0.06 | - |
| Ni | (6) | 5.4±0.4 | - | 4.5±0.1 | - | - | 5.2±1.0 | 4.9±0.6 | 4.6±0.7 | 5.1±0.8 | 8.1±0.2 |
| P% | 0.55±0.02 | 0.53±0.01 | - | 0.50±0.00 | 0.52±0.01 | 0.55±0.01 | 0.56±0.00 | 0.55±0.01 | 0.55±0.01 | 0.56±0.01 | 0.60±0.01 |
| Pb | 1.2±0.2 | 3.4±0.5 | 1.1±0.1 | 2.6±0.3 | - | - | 1.4±0.7 | 1.0±0.9 | <1.5 | 1.4±1.2 | -1.0±0.8 |
| Zn | 50±2 | 42.3±2.4 | 48±3 | 51.5±0.5 | 45.5±1.0 | 49.8±1.3 | 49.3±1.5 | 47±1 | 47±1 | 49±1 | 54±1 |

Table XXII. Literature Survey of Values Found for NBS SRM 1573 Tomato Leaves (μg/g).

| NBS SRM 1573 TOMATO LEAVES | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| ELEMENT | NBS | FOUND | d | e | $i_1$ | $i_2$ | $j_1$ | $j_2$ | $j_3$ | $j_4$ | k |
| Al | (1200) | 747±32 | - | - | - | - | 735±170 | 510±160 | 310±140 | 730±180 | - |
| B | (30) | 36±1 | - | - | - | - | 30±1 | 35±1 | 34±1 | 30±2 | 25.5±1.1 |
| Ca% | 3.00±0.03 | 2.91±0.02 | - | - | 2.60±0.03 | 2.88±0.02 | 3.00±0.08 | 3.30±0.03 | 2.96±0.04 | 3.02±0.08 | 3.41±0.09 |
| Cr | 4.5±0.5 | 3.5±0.1 | - | - | - | - | 4.4±1.2 | 3.0±0.2 | 4.0±0.3 | 4.6±0.7 | 5.9±0.2 |
| Cu | 11±1 | 9.7±0.4 | 9.8±0.3 | 10.4±0.6 | 8.5±0.4 | 9.6±0.5 | 11.7±1.5 | 10.3±0.6 | 10.9±0.8 | 11.2±0.9 | 10.4±0.2 |
| Fe | 690±25 | 547±16 | - | 685±20 | 505±5.6 | 538±3.4 | 697±14 | 544±14 | 509±10 | 694±17 | 568±3 |
| K% | 4.46±0.03 | 4.03±0.14 | - | - | 3.90±0.05 | 4.30±0.09 | 4.38±0.16 | 4.28±0.16 | 4.34±0.16 | 4.28±0.02 | 3.00±0.29 |
| Mg% | (0.70) | 0.64±0.008 | - | - | 0.61±0.01 | 0.68±0.01 | 0.71±0.02 | 0.70±0.01 | 0.68±0.02 | 0.71±0.02 | 0.61±0.06 |
| Mn | 238±7 | 213±5 | 240±4 | 234±5 | 199±1.7 | 220±1.7 | 236±7 | 221±12 | 232±13 | 237±10 | 235±5 |
| Na | - | 554±22 | - | - | 330±10 | 370±10 | 370±25 | - | 390±40 | 370±40 | - |
| Ni | - | 1.4±0.3 | - | - | - | - | 1.1±0.3 | 0.9±0.3 | 1.3±0.6 | 1.1±0.3 | 5.9±0.6 |
| P% | 0.34±0.02 | 0.33±0.005 | - | - | 0.30±0.01 | 0.34±0.01 | 0.34±0.007 | 0.35±0.01 | 0.35±0.01 | 0.34±0.01 | 0.37±0.01 |
| Pb | 6.3±0.3 | 4.5±0.5 | - | 6.1±0.3 | - | - | 6.2±0.8 | 5±2 | 5±3 | 6±1 | 8.3±1.1 |
| Zn | 62±6 | 53±3 | 71±2 | - | 59.0±1.0 | 61.3±1.3 | 61±2 | 61±2 | 61±4 | 62±2 | 73±3 |

Table XXIII. References Corresponding to Tables XX, XXI and XXII.


a) N.R. McQuaker, P.D. Kluckner, G.W. Chong, Anal. Chem. 1979,51,888-895.

b) N.R. McQuaker, D.F. Brown, P.D. Kluckner, Anal. Chem. 1979,51,1082-1084.

c) R.L. Dahlquist, J.W. Knoll, Appl. Spectrosc. 1978,32, 1-33.

d) P. Schramel, Xu-Li-giang, ICP Info. Newsl. 1982,7(9), 429-440.

e) P. Schramel, A. Wolf, R. Seit, B.J. Klose, Fresenius Z. Anal. Chem. 1980,302,62-64.

f) R.C. Munter, R.A. Grande, P.C. Ahn, ICP Info. Newsl. 1979,5(7),368-383.

g) J.B. Jones, Jr., Comm. in Soil Sci. and Plant Analysis 1977,8(4),349-365.

h) R.J. Zasoski, R.G. Burau, Comm. in Soil Sci. and Plant Analysis 1977,8(5),425-436.

i) J.L. Havlin, P.N. Soltanpour, Comm. in Soil Sci. and Plant Analysis 1980,11(10),969-980.

j) A.F. Ward, L.F. Marciello, L. Carrara, V.J. Luciano, Spectrosc. Lett. 1980,13(11),803-831.

k) J.L. Hern, in Applications of Plasma Emission Spectrochemistry, R.M. Barnes,ed., Heyden and Son, Inc., Philadelphia, PA, (1979), pp.23-32.

Table XXIV. Methods of Sample Preparation Corresponding to Tables XX, XXI and XXII.

## Sample Preparation Methods

a) $HNO_3/HClO_4$ or $HNO_3/HF/HClO_4$

b) $HNO_3/HClO_4$ or $HNO_3/HF/HClO_4$

c) (1) ICPQ OES
   (2) ICPQ dry ashed materials in HCl solution
   (3) long term ICPQ
   (4) short ICPQ wet ashed ($HNO_3$-$HClO_4$)
   (5) column 1: Method B with $HNO_3$ 7th, 15:59
   column 2: Method B with $HNO_3$ 11th, 18:59
   column 3: Method C without $HNO_3$ 11th, 19:04
   column 4: Method C without $HNO_3$ 11th, 21:19

d) $HNO_3$ T - controlled autoclave at 160°C for 6 hours

e) $HNO_3$ T - controlled autoclave at 160°C for 6 hours

f) dry ash in muffle furnace at 485°C for 12 hours followed by addition of 10 ml 2N HCl

g) dry ash in muffle furnace at 500°C for 4 hours followed by addition of 20 ml 20% $HNO_3$

h) nitric-perchloric acid wet digestion

i) (1) nitric-perchloric digest
   (2) nitric digest
   (3) dry ashing
   (4) wet ashing

j) (1) multiple determinations over a 1-month period using $HNO_3/HClO_4$ digestion method
   (2) dry ash sample preparation procedure
   (3) nitric acid - hydrogen peroxide procedure
   (4) nitric-perchloric acid procedure

k) $HNO_3/HClO_4$

agrees with those found in the literature. Generally there are some authors who have obtained a value in close agreement to the certified values given by the National Bureau of Standards.

The dry ash technique followed by acid dissolution (2N HCL) was also used by some of the authors listed in Table XXIII. They are represented by columns $c_2$, f, $i_3$ and $j_2$. As can be seen these results all agree well except for lead which was separated and preconcentrated by these authors before analysis.

A scheme which aids visualization of found data to certified values is shown in Figures 17, 18 and 19 for orchard leaves, spinach leaves and tomato leaves. A five-by-five logarithmic plot is drawn of values found in this work versus NBS certified values. Both sets of data are plotted in µg/g. A log-log plot is necessary because the concentrations range from as low as 1 ppm up to 45000 ppm (4.5% content). Ideally the points should fall on a straight line sloped at a $45^{o}$ angle. In all cases, except lead, the other twelve elements fell on or close to this line. As stated previously, to determine lead accurately separation and preconcentration is necessary. Hydride generation of lead should also give better results.

The ICP spectrometer's performance was validated with these three NBS standards and agreement was found to be quite favorable or as expected according to the literature. Now real unknown samples can be analyzed. They are analyzed with

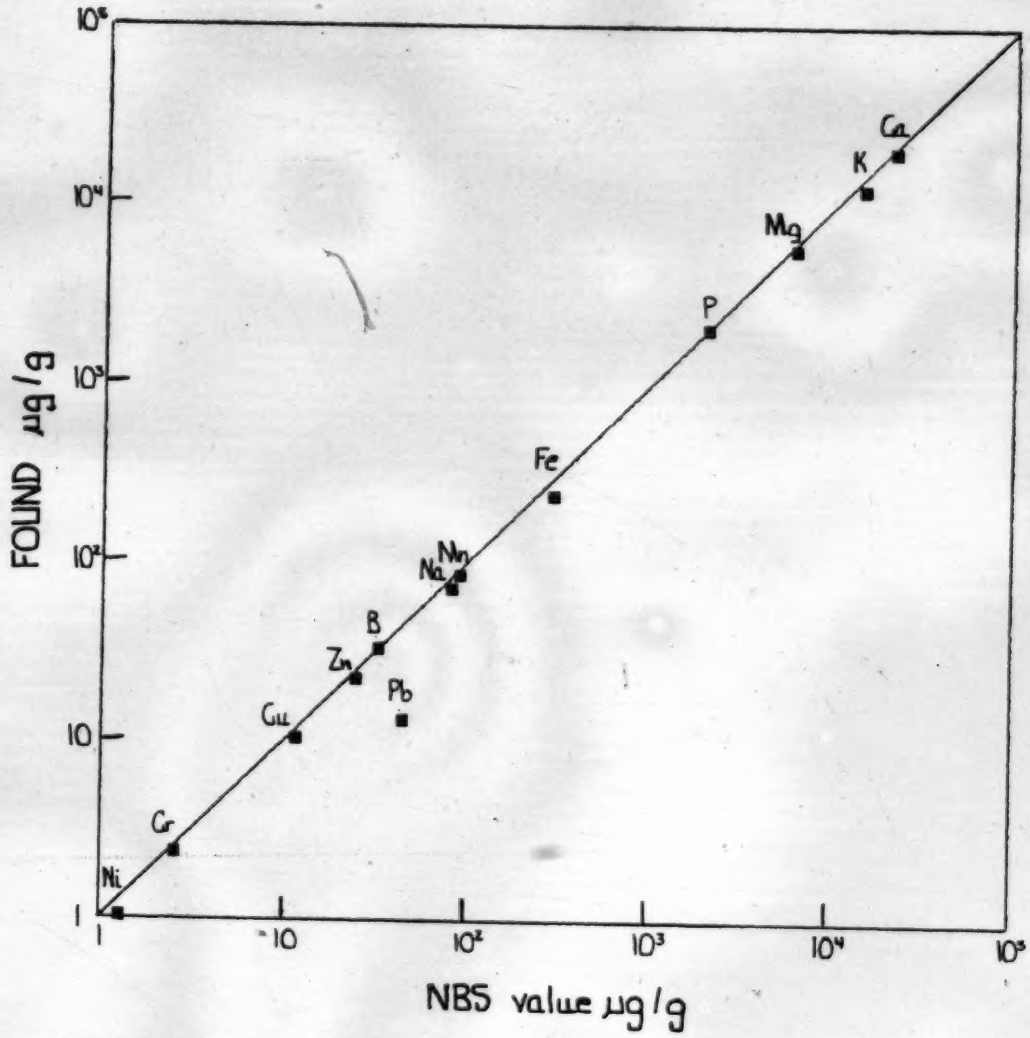


Figure 17. Logarithmic Plot Comparison Of Data Found in This Work to Data Certified by NBS for Orchard Leaves.

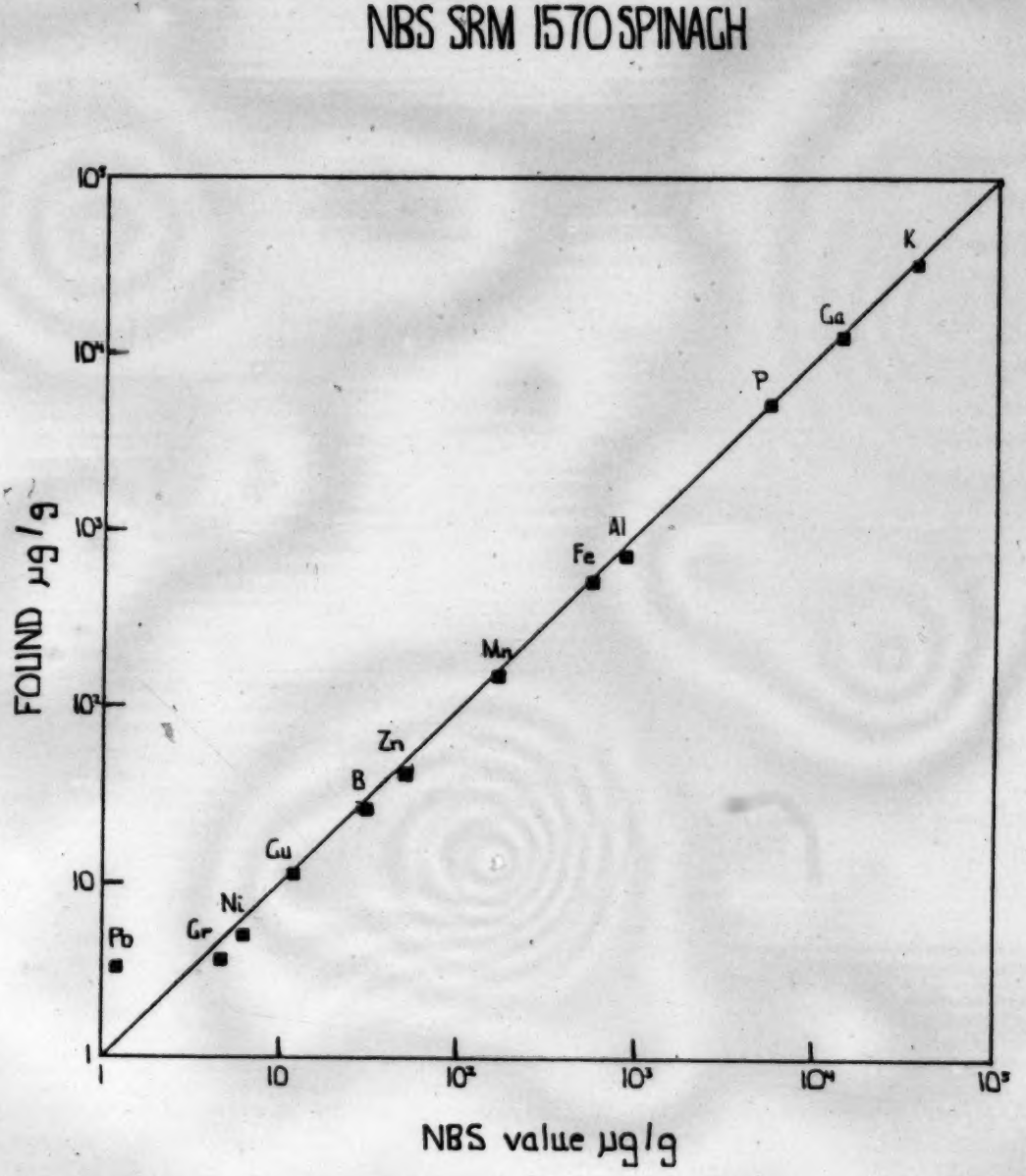


Figure 18. Logarithmic Plot Comparison of Data Found in This Work to Data Certified by NBS for Spinach.

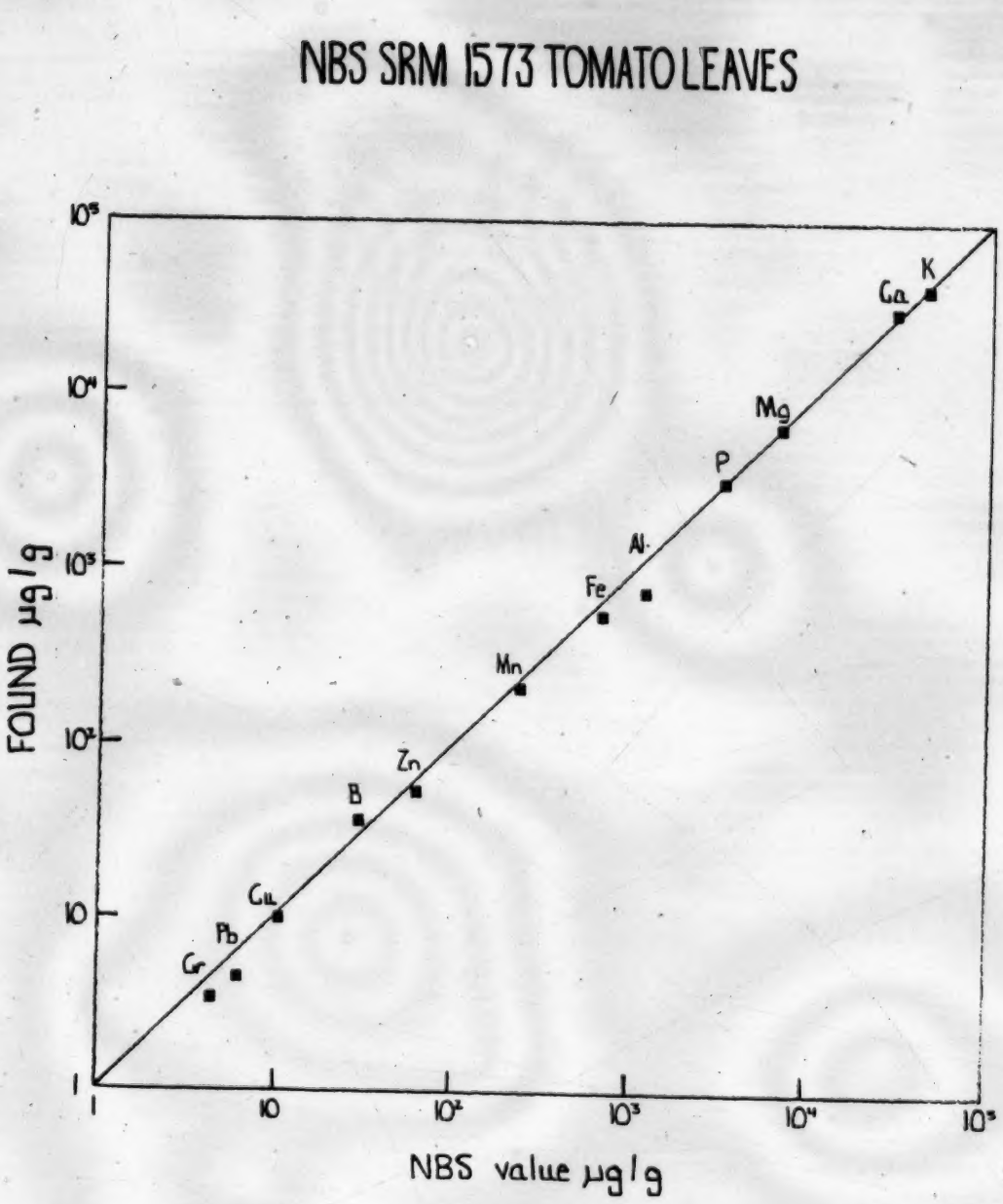


Figure 19. Logarithmic Plot Comparison of Data Found in This Work to Data Certified by NBS for Tomato Leaves.

an NBS standard which acts as an accuracy verification. Analyses were done on garden samples of tomato and lettuce leaves supplied by Maureen Horlick.

The garden samples of tomato and lettuce leaves were washed with distilled-deionized water and sorted for drying in an oven set at 85°C for two to three hours. The samples were then ground and analyzed in a manner similar to the NBS samples - dry ashed in a muffle furnace at 485°C followed by hydrochloric acid dissolution. Oven-dried samples ranging in weights from 0.2 to 0.5 grams (Table XXV) were used.

The tomato leaves were calibrated against NBS tomato leaves SRM 1573 while the lettuce leaves were calibrated against NBS spinach SRM 1570. The results obtained are tabulated in Tables XXVI and XXVII for tomato leaves and lettuce leaves. The results in both tables have been corrected for dilution so the values shown are the actual concentration levels present in the leaves.

The calcium percent content in tomato leaves, Table XXVI, was too high, thus an actual number could not be obtained except in the case of lot 5 sample 0. This sample only weighed 0.1782 grams which did not cause saturation or over-ranging problems to occur in the PMT readout electronics. All of the other tomato leaf samples weighed approximately 0.50 grams, which did cause overranging of the Ca signal.

Cadmium and nickel were both too low for detection. Chromium and lead were measurable only in select cases.

Generally the local tomato leaf samples matched those of

Table XXV. Sample Type, Label, and Weight.

| Sample Type | Lot No. | Sample Label | Weight |
|---|---|---|---|
| Lettuce Leaves | 1 | A | 0.5084 |
| Tomato Leaves | 1 | B | 0.5027 |
| Lettuce Leaves | 2 | C | 0.5028 |
| Lettuce Leaves | 3 | D | 0.3142 |
| Lettuce Leaves | 3 | E | 0.1820 |
| Tomato Leaves | 3 | F | 0.4432 |
| Tomato Leaves | 3 | G | 0.4393 |
| Lettuce Leaves | 4 | H | 0.5062 |
| Lettuce Leaves | 4 | I | 0.4999 |
| Tomato Leaves | 4 | J | 0.5269 |
| Tomato Leaves | 4 | K | 0.5050 |
| Lettuce Leaves | 5 | L | 0.1492 |
| Lettuce Leaves | 5 | M | 0.1593 |
| Tomato Leaves | 5 | N | 0.4100 |
| Tomato Leaves | 5 | O | 0.1782 |
| Tomato Leaves | 5 | P | 0.5036 |

Table XXVI. Analytical Results Obtained for Local Garden Tomato Leaves (μg/g).

| ELE-MENT | NBS 1573 | LOT1 B | LOT3 F | LOT3 G | LOT4 J | LOT4 K | LOT 5 N | LOT 5 O | LOT 5 P |
|---|---|---|---|---|---|---|---|---|---|
| Al | 513 | 79.3 | 149 | 476 | 493 | 251 | 284 | 456 | 451 |
| B | 35.2 | 32.7 | 47.5 | 36.0 | 38.1 | 42.4 | 83.3 | 31.2 | 40.7 |
| Ca% | > | > | > | > | > | > | > | 1.58 | > |
| Cd | < | < | < | < | < | < | < | < | < |
| Cr | 2.75 | 0.37 | < | 0.44 | 0.39 | < | < | < | < |
| Cu | 9.15 | 11.4 | 3.83 | 3.27 | 4.44 | 3.84 | 1.40 | 5.08 | 2.61 |
| Fe | 421 | 126 | 134 | 316 | 357 | 226 | 288 | 319 | 327 |
| K% | 4.00 | 1.78 | 1.60 | 2.33 | 2.30 | 2.32 | 1.79 | 2.90 | 2.19 |
| Mg% | 0.63 | 0.40 | 0.44 | 0.49 | 0.53 | 0.86 | 0.53 | 0.51 | 0.37 |
| Mn | 203 | 20.2 | 28.7 | 38.9 | 75.5 | 76.6 | 121 | 52.8 | 94.3 |
| Na | 378 | 145 | 378 | 500 | 322 | 360 | 242 | 294 | 202 |
| Ni | < | < | < | < | < | < | < | < | < |
| P% | 0.33 | 0.40 | 0.44 | 0.44 | 0.48 | 0.26 | 0.49 | 0.62 | 0.47 |
| Pb | 1.42 | < | < | < | 1.11 | 1.26 | < | < | < |
| Zn | 55.1 | 20.2 | 13.7 | 10.8 | 20.6 | 12.4 | 13.4 | 28.8 | 17.0 |

Reference material used was NBS Tomato Leaves SRM 1573.

Table XXVII. Analytical Results Obtained for Local Garden Lettuce Leaves (µg/g).

| ELE-MENT | NBS 1570 | LOT 1 A | LOT 2 C | LOT 3 D | LOT 3 E | LOT 4 H | LOT 4 I | LOT 5 L | LOT 5 M |
|---|---|---|---|---|---|---|---|---|---|
| Al | 544 | 16.8 | 92.3 | 88.1 | 172 | 132 | 134 | 426 | 235 |
| B | 25.8 | 18.8 | 21.1 | 24.1 | 29.3 | 12.9 | 24.8 | 25.9 | 20.6 |
| Ca% | 1.12 | 0.73 | 1.19 | 1.30 | 1.25 | 0.67 | 1.03 | 1.52 | 1.22 |
| Cd | < | < | < | < | < | < | < | < | < |
| Cr | 2.60 | < | < | < | < | < | < | < | < |
| Cu | 10.3 | 6.87 | 6.50 | 1.69 | 1.39 | 2.71 | 1.61 | 1.61 | 6.01 |
| Fe | 426 | 106 | 85.8 | 91.7 | 135 | 90.9 | 108 | 260 | 150 |
| K% | 3.00 | 4.19 | 4.20 | 6.14 | 6.71 | 2.13 | 3.68 | 3.51 | 3.76 |
| Mg% | 0.78 | 0.35 | 0.31 | 0.28 | 0.33 | 0.11 | 0.22 | 0.27 | 0.24 |
| Mn | 152 | 25.6 | 46.1 | 88.2 | 57.9 | 66.8 | 158 | 199 | 180 |
| Na% | > | 0.16 | 0.14 | 0.20 | 0.10 | 0.01 | 0.02 | 0.13 | 0.05 |
| Ni | 4.05 | < | < | < | < | < | < | < | < |
| P% | 0.52 | 0.61 | 0.52 | 0.68 | 0.41 | 0.22 | 0.31 | 0.23 | 0.35 |
| Pb | 1.74 | < | < | < | < | < | < | < | < |
| Zn | 42.3 | 42.6 | 60.0 | 16.6 | 14.7 | 11.4 | 20.9 | 36.8 | 27.3 |

Reference material used was NBS Spinach SRM 1570.

the NBS reference, though elemental values were generally lower for the local samples. This could be due to differences in climatic conditions, soil composition, species and variety of the plant, age of the tissue, sample size, homogeneity, etc.

Local garden lettuce samples were compared to NBS Spinach. In the real samples Cd, Cr, Ni and Pb were all too low in concentration to be detected. However, the calcium level is lower in this sample type and was measurable.

Five of the samples including NBS Spinach, A, C, H and I weighed approximately 0.50 grams. Sample D weighed 0.3142 grams while samples E, L and M weighed approximately 0.2 grams. As for the tomato leaves, the concentrations were lower than the substance it was referenced with, except for K where the content was appreciably higher. This may be due to the soil or simply difference in sample types used for comparisons. The averages of the garden samples are listed in Table XXVIII with the ICP values for their counterpart reference.

Chemical elements which are known to be essential for plant growth include C, H, O and mineral elements K, Ca, Mg, N, P, S, B, Cl, Cu, Fe, Mn, Mo and Zn (67). Of these 16 elements C, H, O, K, Ca, Mg, N, P and S constitute the macroelements, essential elements required in relatively large amounts. The remaining elements are classified as microelements, essential elements required in relatively small amounts.

Table XXVIII. Summary of Results for Tomato and Lettuce Leaves. All values for garden samples were averaged (µg/g).

| Element | Concentration | | | |
|---|---|---|---|---|
| | Tomato | NBS 1573 | Lettuce | NBS 1570 |
| Al | 330 | 513 | 162 | 544 |
| B | 44.0 | 35.2 | 22.2 | 25.8 |
| Ca% | < | < | 1.11 | 1.12 |
| Cd | < | < | < | < |
| Cr | 0.40 | 2.75 | < | 2.60 |
| Cu | 4.48 | 9.15 | 3.55 | 10.3 |
| Fe | 262 | 421 | 128 | 426 |
| K% | 2.15 | 4.00 | 4.29 | 3.00 |
| Mg% | 0.51 | 0.63 | 0.26 | 0.78 |
| Mn | 63.5 | 203 | 103 | 152 |
| Na | 305 | 378 | 1000 | > |
| Ni | < | < | < | 4.05 |
| P% | 0.45 | 0.33 | 0.42 | 0.52 |
| Pb | 1.18 | 1.42 | < | 1.74 |
| Zn | 17.1 | 55.1 | 28.8 | 42.3 |

The macroelements - K, Ca and Mg - are present in soils as cations - $K^+$, $Ca^{++}$ and $Mg^{++}$, while N, P and S are present in soils as anions $NO_3^-$, $H_2PO_4^-$ and $SO_4^=$. These inorganic ions constitute the macronutrients. The microelements are usually supplied as the following undissociated molecules or ions: $H_3BO_3$ (boric acid), $Cl^-$ (chloride), $Cu^{++}$ (cupric), $Fe^{++}$ (ferrous) or $Fe^{+++}$ (ferric), $Mn^{++}$ (manganous), $MoO_4^=$ (molybdate) and $Zn^{++}$ (zinc).

Of these sixteen elements only nine were analyzed in this study - B, Ca, Cu, Fe, K, Mg, Mn, P and Zn. The macroelements - K, Ca, Mg and P - were present at the percent level for both lettuce and tomato leaves. The microelements - B, Cu, Fe, Mn and Zn - range in concentration from 3 ppm for Cu in lettuce leaves up to maximum of 262 ppm for Fe in tomato leaves (see Table XXVII).

E. Water Analysis

Water samples are relatively easy to analyze as the samples require no pretreatment prior to aspirating into the plasma (68). However, as stated earlier, water samples should be stabilized by the addition of dilute acid. This has been found necessary (64,65,69) as 'rapid changes may occur in the chemical composition of water samples during storage, owing either to the introduction of contaminants from the containers or to selective absorption of metals onto the wall of containers' (69).

Two analyses of waters were run - one on various types

of distilled-deionized waters and the other on well waters. The total element general purpose calibration scheme (Table VI) was used to calibrate the spectrometer for these samples.

A summary of the data collected for the distilled-deionized (DDI) waters is presented in Table XXIX. A brief summary of each sample title is also given. Millipore water is distilled and deionized to a purity of 18 megohms/cc as measured on the gauge provided with the Millipore Milli-Q water purification system. DDI water provided by Dr. Cantwell is distilled with $KMnO_4$ and deionized, while that provided by Dr. Rabenstein is treated with an ion exchange resin bed.

None of the DDI waters were found to contain detectable levels of Li, Na, Sn, In or Ag. The remaining elements were found at relatively trace levels as desired with DDI water. Tap water displays noticeable amounts of Na, K, Mg, Ca, S and Si. However, with just a single distillation these elements were brought down to trace levels. Strontium, P, B and Al exist at low levels in tap water and are removed to much lower levels with a single distillation.

The DDI water provided by Dr. Cantwell does not indicate the presence of excesses of either K or Mn even though $KMnO_4$ was used in the distillation. Thus this water is acceptable for analysis of these elements without fear of cross contamination.

Lead, Ge, Sb, S and Cd were not detected in distilled water, but traces of these elements do appear in the DDI waters. Thus the deionization process may be adding minute quantities of these elements to the water. On the whole,

Table XXIX. Analysis of Waters - Tap Water, Distilled Water and Distilled-Deionized Water(μg/ml).

ANALYSIS OF WATER PURITY WITH VARIOUS METHODS OF DEIONIZATION

DATE OF ANALYSIS: 23-APR-82

| | SAMPLE | LI | NA | K | MG | CA | SR | BA |
|---|---|---|---|---|---|---|---|---|
| 1 | TAP | < 0.0000 | 19.753 | 5.4415 | 6.6864 | 40.326 | 0.2593 | 0.0463 |
| 2 | TAP | < 0.0000 | 10.229 | 5.4940 | 6.7333 | 40.615 | 0.2614 | 0.0473 |
| 3 | DISTD | < 0.0000 | < 0.0000 | 0.0627 | 0.0255 | 0.1152 | 0.0014 | 0.0015 |
| 4 | DISTD | < 0.0000 | < 0.0000 | 0.0943 | 0.0297 | 0.0626 | 0.0009 | 0.0016 |
| 5 | MILLI | < 0.0000 | < 0.0000 | 0.2886 | 0.1252 | 0.0507 | 0.0014 | 0.0043 |
| 6 | MILLI | < 0.0000 | < 0.0000 | 0.0995 | 0.0280 | 0.0189 | 0.0005 | 0.0020 |
| 7 | RABEN | < 0.0000 | < 0.0000 | 0.0890 | 0.0314 | 0.0218 | 0.0005 | 0.0040 |
| 8 | RABEN | < 0.0000 | < 0.0000 | 0.0627 | 0.0238 | 0.0097 | 0.0004 | 0.0024 |
| 9 | CANT | < 0.0000 | < 0.0000 | 0.0470 | 0.0255 | 0.0068 | 0.0004 | 0.0016 |
| 10 | CANT | < 0.0000 | < 0.0000 | < 0.0000 | 0.0188 | < 0.0000 | 0.0001 | 0.0008 |

| | SAMPLE | SN | PB | GE | AS | SB | C | N |
|---|---|---|---|---|---|---|---|---|
| 1 | TAP | < 0.0000 | 0.0180 | 0.0056 | 0.0152 | < 0.0000 | 45.063 | < 0.0000 |
| 2 | TAP | < 0.0000 | 0.0207 | < 0.0000 | 0.0048 | 0.0090 | 33.261 | < 0.0000 |
| 3 | DISTD | < 0.0000 | < 0.0000 | < 0.0000 | 0.0015 | < 0.0000 | 16.311 | < 0.0000 |
| 4 | DISTD | < 0.0000 | < 0.0000 | < 0.0000 | 0.0061 | < 0.0000 | 12.209 | < 0.0000 |
| 5 | MILLI | 0.0121 | 0.0803 | 0.1002 | 0.0563 | 0.0484 | 9.1291 | < 0.0000 |
| 6 | MILLI | < 0.0000 | 0.0093 | 0.0083 | 0.0011 | 0.0189 | 5.4734 | 440.63 |
| 7 | RABEN | < 0.0000 | 0.0145 | 0.0056 | 0.0036 | 0.0074 | 16.041 | < 0.0000 |
| 8 | RABEN | < 0.0000 | 0.0084 | 0.0010 | 0.0032 | < 0.0000 | 16.358 | < 0.0000 |
| 9 | CANT | < 0.0000 | 0.0022 | 0.0074 | 0.0090 | 0.0102 | 14.830 | < 0.0000 |
| 10 | CANT | < 0.0000 | 0.0391 | 0.0304 | 0.0156 | 0.0094 | 15.253 | < 0.0000 |

| | SAMPLE | S | P | TI | ZR | V | CR | MO |
|---|---|---|---|---|---|---|---|---|
| 1 | TAP | 5.1690 | 0.3317 | < 0.0000 | 0.0153 | < 0.0000 | 0.0029 | 0.0027 |
| 2 | TAP | 5.1907 | 0.1925 | < 0.0000 | 0.0171 | < 0.0000 | 0.0044 | 0.0052 |
| 3 | DISTD | < 0.0000 | 0.0606 | < 0.0000 | 0.0158 | < 0.0000 | 0.0008 | 0.0052 |
| 4 | DISTD | < 0.0000 | 0.0841 | 0.0002 | 0.0171 | 0.0002 | 0.0014 | 0.0029 |
| 5 | MILLI | 0.0201 | 0.2233 | 0.0081 | 0.0417 | 0.0136 | 0.0086 | 0.0129 |
| 6 | MILLI | 0.0219 | 0.0137 | 0.0008 | 0.0174 | 0.0019 | 0.0025 | 0.0066 |
| 7 | RABEN | < 0.0000 | 0.0665 | 0.0020 | 0.0189 | 0.0019 | 0.0012 | 0.0085 |
| 8 | RABEN | < 0.0000 | 0.0797 | 0.0023 | 0.0174 | 0.0031 | < 0.0000 | 0.0068 |
| 9 | CANT | 0.0063 | 0.0694 | 0.0007 | 0.0151 | 0.0026 | < 0.0000 | 0.0068 |
| 10 | CANT | 0.0069 | 0.0636 | 0.0008 | 0.0083 | 0.0007 | 0.0022 | 0.0091 |

Table XXIX. Continued.

| | SAMPLE | MN | FE | NI | CU | ZN | CD1 | CD2 |
|---|---|---|---|---|---|---|---|---|
| 1 | TAP | 0.0035 | 0.0123 | 0.0130 | 0.0001 | 0.0062 | 0.0026 | 0.0002 |
| 2 | TAP | 0.0032 | 0.0099 | 0.0125 | 0.0014 | 0.0050 | 0.0015 | 0.0006 |
| 3 | DISTD | < 0.0000 | 0.0015 | < 0.0000 | 0.0021 | 0.0071 | 0.0006 | < 0.0000 |
| 4 | DISTD | 0.0002 | 0.0019 | 0.0001 | 0.0024 | 0.0096 | < 0.0000 | < 0.0000 |
| 5 | MILLI | 0.0026 | 0.0129 | 0.0365 | 0.0124 | 0.0029 | 0.0073 | 0.0033 |
| 6 | MILLI | 0.0005 | 0.0024 | 0.0094 | 0.0009 | 0.0006 | 0.0017 | 0.0002 |
| 7 | RABEN | 0.0009 | 0.0027 | 0.0110 | 0.0014 | 0.0129 | 0.0028 | 0.0006 |
| 8 | RABEN | 0.0006 | 0.0028 | 0.0099 | 0.0011 | 0.0072 | 0.0014 | 0.0010 |
| 9 | CANT | 0.0008 | 0.0024 | 0.0032 | 0.0004 | 0.0010 | 0.0003 | < 0.0000 |
| 10 | CANT | 0.0012 | 0.0010 | 0.0182 | < 0.0000 | 0.0031 | 0.0024 | 0.0015 |

| | SAMPLE | HG | B | AL | IN | SI | AG |
|---|---|---|---|---|---|---|---|
| 1 | TAP | 0.0204 | 0.1428 | 0.5911 | 0.0121 | 2.5370 | < 0.0000 |
| 2 | TAP | 0.0096 | 0.1246 | 0.6032 | < 0.0000 | 2.5694 | < 0.0000 |
| 3 | DISTD | 0.0213 | 0.0361 | 0.0565 | < 0.0000 | 0.0346 | < 0.0000 |
| 4 | DISTD | 0.0230 | 0.0192 | 0.0673 | < 0.0000 | 0.0201 | < 0.0000 |
| 5 | MILLI | 0.0455 | 0.0342 | 0.2003 | 0.0617 | 0.0791 | 0.0059 |
| 6 | MILLI | 0.0332 | 0.0067 | 0.0525 | < 0.0000 | 0.0209 | < 0.0000 |
| 7 | RABEN | 0.0304 | 0.0136 | 0.0754 | < 0.0000 | 0.0152 | < 0.0000 |
| 8 | RABEN | 0.0347 | 0.0155 | 0.0807 | < 0.0000 | 0.0233 | < 0.0000 |
| 9 | CANT | 0.0328 | 0.0219 | 0.0471 | < 0.0000 | 0.0573 | < 0.0000 |
| 10 | CANT | 0.0328 | 0.0203 | 0.0539 | < 0.0000 | 0.0508 | < 0.0000 |

TAP = TAP WATER FROM ROOM W318
DISTD = DISTILLED WATER ; MILLI = MILLIPORE ION EXCHANGE
CANT = CANTWELL KMNO4 DEIONIZED ; RABEN = RABENSTEIN ION RESIN

these methods of deionization are comparable and a few elements are present in such minute quantities that no problems of contamination are expected or were found on using DDI waters in sample preparation.

A selection of well waters was analyzed along with tap, distilled and Millipore DDI waters. The raw data is tabulated and displayed in Table XXX for all 34 channels. Each type of water was run in triplicate and a summary of the means is given in Table XXXI.

Water can be treated via filtration - passage of water through a porous medium to remove matter held in suspension, sedimentation - separation of solids from the water by gravity and softening - removal of Ca and Mg ions from the water as solids, viz., calcium carbonate and magnesium hydroxide. Water softening incorporates both sedimentation and filtration for the removal of these precipitates (69).

Well water 1A underwent no treatment. This is due to the Na and S levels being extremely high so that no treatment is possible. Because the S level is so high the people with this well must specially bring in water for both cooking and drinking purposes. This well water is also relatively soft.

Water hardness is due primarily to the presence of ions of Ca and Mg and is 'expressed as the equivalent quantity of calcium carbonate' ($CaCO_3$). Water with less than 75 mg $CaCO_3$ per liter (30 ppm Ca) is generally considered soft and above 75 mg per liter as hard' (69).

Well water 1A was previously stated as being considered

Table XXX. Raw Data for Analysis of Well Waters (µg/ml).

COMPARISON OF TAP DISTILLED DDI WELL WATERS

DATE OF ANALYSIS: 27-AUG-82

| | SAMPLE | LI | NA | K | MG | CA | SR | BA |
|---|---|---|---|---|---|---|---|---|
| 1 | TAP | < 0.0071 | 6.2183 | 0.7695 | 12.883 | 47.806 | 0.3057 | 0.0218 |
| 2 | TAP | < 0.0071 | 6.2051 | 0.7603 | 12.833 | 47.676 | 0.3049 | 0.0217 |
| 3 | TAP | < 0.0071 | 6.1748 | 0.7970 | 12.836 | 47.524 | 0.3031 | 0.0222 |
| 4 | D H2O | < 0.0071 | < 0.2025 | < 0.4702 | < 0.0831 | 0.0648 | < 0.0015 | < 0.0038 |
| 5 | D H2O | < 0.0071 | < 0.2025 | < 0.4702 | 0.1123 | < 0.0365 | < 0.0015 | < 0.0038 |
| 6 | D H2O | < 0.0071 | < 0.2025 | < 0.4702 | < 0.0831 | < 0.0365 | < 0.0015 | < 0.0038 |
| 7 | DDI | < 0.0071 | < 0.2025 | < 0.4702 | < 0.0831 | < 0.0365 | < 0.0015 | < 0.0038 |
| 8 | DDI | < 0.0071 | < 0.2025 | < 0.4702 | < 0.0831 | < 0.0365 | < 0.0015 | < 0.0038 |
| 9 | DDI | < 0.0071 | < 0.2025 | < 0.4702 | < 0.0831 | < 0.0365 | < 0.0015 | < 0.0038 |
| 10 | 1A | 0.0349 | 291.98 | 0.6316 | 0.5178 | 3.8467 | 0.0199 | < 0.0038 |
| 11 | 1A | 0.0356 | 290.73 | 0.6592 | 0.5088 | 3.8417 | 0.0201 | < 0.0038 |
| 12 | 1A | 0.0356 | 287.74 | 0.6776 | 0.5148 | 3.8242 | 0.0194 | < 0.0038 |
| 13 | 2A | 0.0657 | 364.51 | 0.5214 | 0.2109 | 3.2335 | 0.0179 | 0.0158 |
| 14 | 2A | 0.0679 | 363.69 | 0.5949 | 0.2209 | 3.2582 | 0.0187 | 0.0216 |
| 15 | 2A | 0.0644 | 361.84 | 0.5581 | 0.2049 | 3.2388 | 0.0184 | 0.0217 |
| 16 | 2B | 0.0676 | 363.48 | 0.5673 | 0.2538 | 3.2496 | 0.0198 | 0.0226 |
| 17 | 2B | 0.0676 | 360.51 | 0.5673 | 0.2597 | 3.2433 | 0.0195 | 0.0228 |
| 18 | 2B | 0.0647 | 356.18 | 0.4846 | 0.2548 | 3.1948 | 0.0185 | 0.0218 |
| 19 | 3A | 0.0598 | 64.662 | 3.4434 | 14.824 | 68.373 | 0.6521 | 0.0815 |
| 20 | 3A | 0.0676 | 64.643 | 3.5169 | 14.904 | 68.522 | 0.6534 | 0.0798 |
| 21 | 3A | 0.0673 | 64.075 | 3.4893 | 14.802 | 68.012 | 0.6473 | 0.0784 |
| 22 | 3B | 0.0913 | 189.21 | < 0.4702 | < 0.0831 | 0.1618 | < 0.0015 | < 0.0038 |
| 23 | 3B | 0.0916 | 188.63 | 0.4754 | < 0.0831 | 0.1386 | < 0.0015 | < 0.0038 |
| 24 | 3B | 0.0919 | 187.17 | < 0.4702 | < 0.0831 | 0.1351 | < 0.0015 | < 0.0038 |
| 25 | 4A | 0.0362 | 20.736 | 2.4418 | 18.200 | 81.478 | 0.5656 | 0.1586 |
| 26 | 4A | 0.0365 | 20.634 | 2.4510 | 18.205 | 81.475 | 0.5648 | 0.1593 |
| 27 | 4A | 0.0339 | 20.471 | 2.3407 | 18.006 | 80.502 | 0.5581 | 0.1573 |
| 28 | 5A | 0.0472 | 41.222 | 2.9931 | 18.172 | 76.207 | 0.6506 | 0.1598 |
| 29 | 5A | 0.0456 | 41.245 | 3.0942 | 18.144 | 76.175 | 0.6512 | 0.1609 |
| 30 | 5A | 0.0482 | 40.840 | 3.1402 | 18.039 | 75.586 | 0.6452 | 0.1595 |
| 31 | 5B | < 0.0071 | 173.96 | 1.1830 | 0.1262 | 0.4655 | < 0.0015 | < 0.0038 |
| 32 | 5B | < 0.0071 | 172.96 | 1.2565 | 0.1372 | 0.4478 | < 0.0015 | < 0.0038 |
| 33 | 5B | < 0.0071 | 171.59 | 1.1646 | 0.0953 | 0.4364 | < 0.0015 | < 0.0038 |
| 34 | 7A | 0.0459 | 244.12 | 1.2289 | 1.1973 | 7.2754 | 0.0575 | 0.0078 |
| 35 | 7A | 0.0462 | 243.32 | 1.2657 | 1.1565 | 7.2821 | 0.0577 | 0.0103 |
| 36 | 7A | 0.0462 | 241.49 | 1.3300 | 1.1883 | 7.2406 | 0.0570 | 0.0103 |
| 37 | 7B | 0.0547 | 242.62 | 11.300 | 1.2860 | 6.9831 | 0.0535 | < 0.0038 |
| 38 | 7B | 0.0530 | 243.97 | 11.382 | 1.3079 | 7.0423 | 0.0543 | < 0.0038 |
| 39 | 7B | 0.0553 | 241.11 | 11.235 | 1.2989 | 6.9672 | 0.0532 | < 0.0038 |

Table XXX. Continued.

| | SAMPLE | SN | PB | GE | AS | SB | C | N |
|---|---|---|---|---|---|---|---|---|
| 1 | TAP | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 931.91 | 13.296 |
| 2 | TAP | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 964.99 | < 0.0000 |
| 3 | TAP | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 865.04 | < 0.0000 |
| 4 | D H2O | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 434.53 | < 0.0000 |
| 5 | D H2O | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 405.82 | < 0.0000 |
| 6 | D H2O | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 388.55 | < 0.0000 |
| 7 | DDI | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 339.85 | < 0.0000 |
| 8 | DDI | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 335.85 | < 0.0000 |
| 9 | DDI | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 333.31 | < 0.0000 |
| 10 | 1A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1487.5 | < 0.0000 |
| 11 | 1A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1490.5 | < 0.0000 |
| 12 | 1A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1394.6 | < 0.0000 |
| 13 | 2A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1786.4 | < 0.0000 |
| 14 | 2A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1625.7 | < 0.0000 |
| 15 | 2A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1553.1 | < 0.0000 |
| 16 | 2B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1578.5 | < 0.0000 |
| 17 | 2B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1499.6 | < 0.0000 |
| 18 | 2B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1367.9 | < 0.0000 |
| 19 | 3A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 2454.1 | < 0.0000 |
| 20 | 3A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 2324.7 | < 0.0000 |
| 21 | 3A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 2079.7 | < 0.0000 |
| 22 | 3B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 2189.8 | < 0.0000 |
| 23 | 3B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 2028.1 | < 0.0000 |
| 24 | 3B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1884.5 | < 0.0000 |
| 25 | 4A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1878.2 | < 0.0000 |
| 26 | 4A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1700.4 | < 0.0000 |
| 27 | 4A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1531.4 | < 0.0000 |
| 28 | 5A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1333.0 | < 0.0000 |
| 29 | 5A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1252.1 | < 0.0000 |
| 30 | 5A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1171.6 | < 0.0000 |
| 31 | 5B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 2001.2 | < 0.0000 |
| 32 | 5B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1850.9 | < 0.0000 |
| 33 | 5B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1700.8 | < 0.0000 |
| 34 | 7A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1023.0 | < 0.0000 |
| 35 | 7A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 990.43 | < 0.0000 |
| 36 | 7A | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 927.19 | < 0.0000 |
| 37 | 7B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1261.9 | < 0.0000 |
| 38 | 7B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1194.3 | < 0.0000 |
| 39 | 7B | < 0.0497 | < 0.0268 | < 0.2863 | < 0.1076 | < 0.1363 | 1128.0 | < 0.0000 |

Table XXX. Continued.

| | SAMPLE | S | P | TI | ZR | V | CR | MO |
|---|---|---|---|---|---|---|---|---|
| 1 | TAP | 2.9794 | < 0.2905 | < 0.0048 | 0.7468 | < 0.0174 | < 0.0218 | < 0.0378 |
| 2 | TAP | 2.9459 | < 0.2905 | < 0.0048 | 0.7347 | < 0.0174 | < 0.0218 | < 0.0378 |
| 3 | TAP | 2.9318 | < 0.2905 | 0.0055 | 0.7564 | < 0.0174 | < 0.0218 | < 0.0378 |
| 4 | D H2O | < 0.1331 | < 0.2905 | < 0.0048 | 0.7576 | < 0.0174 | < 0.0218 | < 0.0378 |
| 5 | D H2O | < 0.1331 | < 0.2905 | 0.0098 | 0.7974 | < 0.0174 | < 0.0218 | < 0.0378 |
| 6 | D H2O | < 0.1331 | < 0.2905 | < 0.0048 | 0.7492 | < 0.0174 | < 0.0218 | < 0.0378 |
| 7 | DDI | < 0.1331 | < 0.2905 | 0.0053 | 0.7576 | < 0.0174 | < 0.0218 | < 0.0378 |
| 8 | DDI | < 0.1331 | < 0.2905 | 0.0078 | 0.7552 | < 0.0174 | < 0.0218 | < 0.0378 |
| 9 | DDI | < 0.1331 | < 0.2905 | 0.0059 | 0.7588 | < 0.0174 | < 0.0218 | < 0.0378 |
| 10 | 1A | 3.3760 | < 0.2905 | < 0.0048 | 0.7070 | < 0.0174 | < 0.0218 | < 0.0378 |
| 11 | 1A | 3.3707 | < 0.2905 | < 0.0048 | 0.7203 | < 0.0174 | < 0.0218 | < 0.0378 |
| 12 | 1A | 3.3073 | < 0.2905 | < 0.0048 | 0.7287 | < 0.0174 | < 0.0218 | < 0.0378 |
| 13 | 2A | < 0.1331 | < 0.2905 | < 0.0048 | 0.7130 | < 0.0174 | < 0.0218 | < 0.0378 |
| 14 | 2A | < 0.1331 | < 0.2905 | < 0.0048 | 0.7323 | < 0.0174 | < 0.0218 | < 0.0378 |
| 15 | 2A | < 0.1331 | < 0.2905 | < 0.0048 | 0.7263 | < 0.0174 | < 0.0218 | < 0.0378 |
| 16 | 2B | < 0.1331 | < 0.2905 | < 0.0048 | 0.7010 | < 0.0174 | < 0.0218 | < 0.0378 |
| 17 | 2B | < 0.1331 | < 0.2905 | < 0.0048 | 0.7263 | < 0.0174 | < 0.0218 | < 0.0378 |
| 18 | 2B | < 0.1331 | < 0.2905 | < 0.0048 | 0.7239 | < 0.0174 | < 0.0218 | < 0.0378 |
| 19 | 3A | 0.5997 | < 0.2905 | < 0.0048 | 0.6974 | < 0.0174 | < 0.0218 | < 0.0378 |
| 20 | 3A | 0.5991 | < 0.2905 | < 0.0048 | 0.7263 | < 0.0174 | < 0.0218 | < 0.0378 |
| 21 | 3A | 0.5944 | < 0.2905 | < 0.0048 | 0.7287 | < 0.0174 | < 0.0218 | < 0.0378 |
| 22 | 3B | 0.5777 | < 0.2905 | < 0.0048 | 0.7227 | < 0.0174 | < 0.0218 | < 0.0378 |
| 23 | 3B | 0.5741 | < 0.2905 | 0.0051 | 0.7287 | < 0.0174 | < 0.0218 | < 0.0378 |
| 24 | 3B | 0.5784 | < 0.2905 | < 0.0048 | 0.7323 | < 0.0174 | < 0.0218 | < 0.0378 |
| 25 | 4A | 0.6516 | < 0.2905 | < 0.0048 | 0.7335 | < 0.0174 | < 0.0218 | < 0.0378 |
| 26 | 4A | 0.6491 | < 0.2905 | 0.0071 | 0.7359 | < 0.0174 | < 0.0218 | < 0.0378 |
| 27 | 4A | 0.6409 | < 0.2905 | 0.0057 | 0.7299 | < 0.0174 | < 0.0218 | < 0.0378 |
| 28 | 5A | 0.6506 | < 0.2905 | 0.0080 | 0.7407 | < 0.0174 | < 0.0218 | < 0.0378 |
| 29 | 5A | 0.6534 | < 0.2905 | 0.0071 | 0.7311 | < 0.0174 | < 0.0218 | < 0.0378 |
| 30 | 5A | 0.6446 | < 0.2905 | 0.0055 | 0.7468 | < 0.0174 | < 0.0218 | < 0.0378 |
| 31 | 5B | 0.5324 | < 0.2905 | < 0.0048 | 0.7359 | < 0.0174 | < 0.0218 | < 0.0378 |
| 32 | 5B | 0.5296 | < 0.2905 | 0.0075 | 0.7395 | < 0.0174 | < 0.0218 | < 0.0378 |
| 33 | 5B | 0.5239 | < 0.2905 | 0.0073 | 0.7167 | < 0.0174 | < 0.0218 | < 0.0378 |
| 34 | 7A | 1.3456 | < 0.2905 | 0.0075 | 0.7275 | < 0.0174 | < 0.0218 | < 0.0378 |
| 35 | 7A | 1.3375 | < 0.2905 | 0.0067 | 0.7335 | < 0.0174 | < 0.0218 | < 0.0378 |
| 36 | 7A | 1.3345 | < 0.2905 | 0.0086 | 0.7383 | < 0.0174 | < 0.0218 | < 0.0378 |
| 37 | 7B | 1.4075 | < 0.2905 | 0.0067 | 0.7395 | < 0.0174 | < 0.0218 | < 0.0378 |
| 38 | 7B | 1.4051 | < 0.2905 | 0.0084 | 0.7444 | < 0.0174 | < 0.0218 | < 0.0378 |
| 39 | 7B | 1.3829 | < 0.2905 | 0.0096 | 0.7636 | < 0.0174 | < 0.0218 | < 0.0378 |

Table XXX. Continued.

| | SAMPLE | MN | FE | NI | CU | ZN | CD1 | CD2 |
|---|---|---|---|---|---|---|---|---|
| 1 | TAP | < 0.0089 | < 0.0128 | < 0.0355 | 0.0590 | 0.0975 | < 0.0149 | < 0.0213 |
| 2 | TAP | < 0.0089 | < 0.0128 | < 0.0355 | 0.0495 | 0.1059 | < 0.0149 | < 0.0213 |
| 3 | TAP | < 0.0089 | < 0.0128 | < 0.0355 | 0.0488 | 0.1102 | < 0.0149 | < 0.0213 |
| 4 | D H2O | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 5 | D H2O | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | 0.0220 |
| 6 | D H2O | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 7 | DDI | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 8 | DDI | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 9 | DDI | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 10 | 1A | < 0.0089 | 0.0997 | < 0.0355 | 0.0816 | < 0.0200 | < 0.0149 | < 0.0213 |
| 11 | 1A | < 0.0089 | 0.0989 | < 0.0355 | 0.0827 | < 0.0200 | < 0.0149 | < 0.0213 |
| 12 | 1A | < 0.0089 | 0.0971 | < 0.0355 | 0.0830 | < 0.0200 | < 0.0149 | < 0.0213 |
| 13 | 2A | 0.0109 | 0.3955 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 14 | 2A | 0.0115 | 0.3930 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 15 | 2A | 0.0114 | 0.3852 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 16 | 2B | 0.0136 | 0.1283 | < 0.0355 | 0.0703 | < 0.0200 | < 0.0149 | < 0.0213 |
| 17 | 2B | 0.0136 | 0.1254 | < 0.0355 | 0.0765 | < 0.0200 | < 0.0149 | < 0.0213 |
| 18 | 2B | 0.0137 | 0.1244 | < 0.0355 | 0.0714 | < 0.0200 | < 0.0149 | < 0.0213 |
| 19 | 3A | 0.3721 | 3.8256 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 20 | 3A | 0.3736 | 3.7455 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 21 | 3A | 0.3702 | 3.5516 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 22 | 3B | < 0.0089 | 0.0247 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 23 | 3B | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 24 | 3B | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 25 | 4A | 0.1477 | 0.2711 | < 0.0355 | 0.0725 | < 0.0200 | < 0.0149 | < 0.0213 |
| 26 | 4A | 0.1479 | 0.1695 | < 0.0355 | 0.0608 | < 0.0200 | < 0.0149 | < 0.0213 |
| 27 | 4A | 0.1458 | 0.1772 | < 0.0355 | 0.0666 | < 0.0200 | < 0.0149 | < 0.0213 |
| 28 | 5A | 0.3262 | 1.2793 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 29 | 5A | 0.3269 | 1.2617 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 30 | 5A | 0.3246 | 1.2354 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 31 | 5B | < 0.0089 | 0.0170 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 32 | 5B | < 0.0089 | 0.0160 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 33 | 5B | < 0.0089 | 0.0159 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 34 | 7A | 0.0649 | 0.5380 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 35 | 7A | 0.0650 | 0.5384 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 36 | 7A | 0.0648 | 0.5319 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 37 | 7B | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | < 0.0200 | < 0.0149 | < 0.0213 |
| 38 | 7B | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | 0.0206 | < 0.0149 | < 0.0213 |
| 39 | 7B | < 0.0089 | < 0.0128 | < 0.0355 | < 0.0428 | 0.0210 | < 0.0149 | < 0.0213 |

Table XXX. Continued.

| | SAMPLE | HG | B | AL | IN | SI | AG |
|---|---|---|---|---|---|---|---|
| 1 | TAP | < 0.2678 | 0.1035 | < 0.3991 | < 0.2736 | 1.6903 | < 0.0199 |
| 2 | TAP | < 0.2678 | 0.0954 | < 0.3991 | < 0.2736 | 1.6825 | 0.7488 |
| 3 | TAP | < 0.2678 | 0.0942 | < 0.3991 | < 0.2736 | 1.7031 | < 0.0199 |
| 4 | D H20 | < 0.2678 | 0.0762 | < 0.3991 | < 0.2736 | < 0.1689 | < 0.0199 |
| 5 | D H20 | < 0.2678 | 0.0748 | < 0.3991 | < 0.2736 | < 0.1689 | < 0.0199 |
| 6 | D H20 | < 0.2678 | 0.0683 | < 0.3991 | < 0.2736 | < 0.1689 | < 0.0199 |
| 7 | DDI | < 0.2678 | 0.0594 | < 0.3991 | < 0.2736 | < 0.1689 | < 0.0199 |
| 8 | DDI | < 0.2678 | 0.0584 | < 0.3991 | < 0.2736 | < 0.1689 | < 0.0199 |
| 9 | DDI | < 0.2678 | 0.0585 | < 0.3991 | < 0.2736 | < 0.1689 | < 0.0199 |
| 10 | 1A | < 0.2678 | 0.1747 | < 0.3991 | < 0.2736 | 3.5263 | < 0.0199 |
| 11 | 1A | < 0.2678 | 0.1653 | < 0.3991 | < 0.2736 | 3.5185 | < 0.0199 |
| 12 | 1A | < 0.2678 | 0.1667 | < 0.3991 | < 0.2736 | 3.4880 | < 0.0199 |
| 13 | 2A | < 0.2678 | 0.4336 | < 0.3991 | < 0.2736 | 3.4655 | < 0.0199 |
| 14 | 2A | < 0.2678 | 0.4324 | < 0.3991 | < 0.2736 | 3.4645 | < 0.0199 |
| 15 | 2A | < 0.2678 | 0.4276 | < 0.3991 | < 0.2736 | 3.4380 | < 0.0199 |
| 16 | 2B | < 0.2678 | 0.4093 | < 0.3991 | < 0.2736 | 3.4115 | < 0.0199 |
| 17 | 2B | < 0.2678 | 0.4095 | < 0.3991 | < 0.2736 | 3.4036 | < 0.0199 |
| 18 | 2B | < 0.2678 | 0.4078 | < 0.3991 | < 0.2736 | 3.3643 | < 0.0199 |
| 19 | 3A | < 0.2678 | 0.1984 | < 0.3991 | < 0.2736 | 6.5612 | < 0.0199 |
| 20 | 3A | < 0.2678 | 0.2039 | < 0.3991 | < 0.2736 | 6.5877 | < 0.0199 |
| 21 | 3A | < 0.2678 | 0.2045 | < 0.3991 | < 0.2736 | 6.5327 | < 0.0199 |
| 22 | 3B | < 0.2678 | 0.2245 | < 0.3991 | < 0.2736 | 7.1179 | < 0.0199 |
| 23 | 3B | < 0.2678 | 0.2229 | < 0.3991 | < 0.2736 | 7.1080 | < 0.0199 |
| 24 | 3B | < 0.2678 | 0.2188 | < 0.3991 | < 0.2736 | 7.0609 | < 0.0199 |
| 25 | 4A | < 0.2678 | 0.1008 | < 0.3991 | < 0.2736 | 7.4016 | < 0.0199 |
| 26 | 4A | < 0.2678 | 0.1052 | < 0.3991 | < 0.2736 | 7.3928 | < 0.0199 |
| 27 | 4A | < 0.2678 | 0.0967 | < 0.3991 | < 0.2736 | 7.3093 | < 0.0199 |
| 28 | 5A | < 0.2678 | 0.1421 | < 0.3991 | < 0.2736 | 7.0933 | < 0.0199 |
| 29 | 5A | < 0.2678 | 0.1418 | < 0.3991 | < 0.2736 | 7.0884 | < 0.0199 |
| 30 | 5A | < 0.2678 | 0.1426 | < 0.3991 | < 0.2736 | 7.0589 | < 0.0199 |
| 31 | 5B | < 0.2678 | 0.1435 | < 0.3991 | < 0.2736 | 6.9244 | < 0.0199 |
| 32 | 5B | < 0.2678 | 0.1450 | < 0.3991 | < 0.2736 | 6.8969 | < 0.0199 |
| 33 | 5B | < 0.2678 | 0.1427 | < 0.3991 | < 0.2736 | 6.8380 | < 0.0199 |
| 34 | 7A | < 0.2678 | 0.2663 | < 0.3991 | < 0.2736 | 4.4512 | < 0.0199 |
| 35 | 7A | < 0.2678 | 0.2699 | < 0.3991 | < 0.2736 | 4.4286 | < 0.0199 |
| 36 | 7A | < 0.2678 | 0.2678 | < 0.3991 | < 0.2736 | 4.4129 | < 0.0199 |
| 37 | 7B | < 0.2678 | 0.2887 | < 0.3991 | < 0.2736 | 4.6584 | < 0.0199 |
| 38 | 7B | < 0.2678 | 0.2935 | < 0.3991 | < 0.2736 | 4.6888 | < 0.0199 |
| 39 | 7B | < 0.2678 | 0.2934 | < 0.3991 | < 0.2736 | 4.6603 | < 0.0199 |

WELLWATERS AS SUPPLIED BY MAUREEN HORLICK

Table XXXI. Averaged Elemental Concentrations for the Well Water Analysis(μg/ml).

1A : No Treatment.
2A→2B: Sedimentation Tank.
3A→3B: Water Softener.
4A : No Treatment.
5A→5B: Water Softener.
7A→7B: Sedimentation Tank.

| ELEMENT | TAP WATER | DISTILLED WATER | DEIONIZED WATER | WELL WATER 1A | 2A | 2B | 3A | 3B | 4A | 5A | 5B | 7A | 7B |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | < | < | < | 0.04 | 0.07 | 0.07 | 0.06 | 0.09 | 0.04 | 0.05 | < | 0.05 | 0.05 |
| Na | 6.20 | 0.01 | < | 290 | 363 | 360 | 64.5 | 188 | 20.6 | 41.1 | 173 | 243 | 243 |
| K | 0.78 | < | < | 0.66 | 0.56 | 0.54 | 3.48 | 0.45 | 2.41 | 3.08 | 1.20 | 1.27 | 11.3 |
| Mg | 12.8 | 0.08 | 0.05 | 0.51 | 0.21 | 0.26 | 14.8 | 0.07 | 18.1 | 18.1 | 0.12 | 1.18 | 1.30 |
| Ca | 47.7 | < | < | 3.84 | 3.24 | 3.23 | 68.3 | < | 81.2 | 76.0 | 0.45 | 7.27 | 7.00 |
| Sr | 0.30 | < | < | 0.02 | < | 0.02 | 0.65 | < | 0.56 | 0.65 | < | 0.06 | 0.05 |
| Ba | 0.02 | < | < | < | 0.02 | 0.02 | 0.08 | < | 0.16 | 0.16 | < | 0.01 | < |
| Sn | < | < | < | < | < | < | 0.02 | < | < | < | < | < | < |
| Pb | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Ge | < | < | < | < | < | < | < | < | < | < | < | < | < |
| As | < | < | < | < | < | < | < | < | < | < | < | < | < |
| Sb | < | < | < | < | < | < | < | < | < | < | < | < | < |
| C | - | - | - | - | - | - | - | - | - | - | - | - | - |
| N | - | - | - | - | - | - | - | - | - | - | - | - | - |
| S | 2.95 | < | < | 3.35 | < | < | 0.60 | 0.58 | 0.65 | 0.65 | 0.53 | 1.34 | 1.40 |
| P | < | < | < | < | < | < | < | < | < | < | < | < | < |
| Ti | 0.00 | 0.01 | 0.01 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Zr | 0.75 | 0.77 | 0.76 | 0.72 | 0.72 | 0.72 | 0.72 | 0.73 | 0.73 | 0.73 | 0.74 | 0.73 | 0.75 |
| V | < | < | < | < | < | < | < | < | < | < | < | < | < |
| Cr | < | < | < | < | < | < | < | < | < | < | < | < | < |
| Mo | < | < | < | 0.03 | < | < | < | < | < | < | < | < | < |
| Mn | < | < | < | < | < | < | < | < | < | < | < | 0.02 | < |
| Fe | < | < | < | < | < | < | 0.37 | < | < | 0.33 | < | < | < |
| Ni | < | < | < | < | 0.39 | < | 3.71 | < | < | 1.26 | < | 0.54 | < |
| Cu | 0.05 | < | < | 0.08 | < | < | < | < | < | < | < | < | < |
| Zn | 0.10 | < | < | < | < | 0.07 | < | < | 0.07 | < | < | < | < |
| Cd | < | < | < | < | < | < | < | < | < | < | < | < | < |
| Hg | 0.05 | 0.04 | 0.03 | 0.04 | 0.04 | 0.06 | 0.09 | 0.06 | 0.05 | 0.05 | 0.06 | 0.05 | 0.05 |
| B | 0.10 | 0.07 | 0.06 | 0.17 | 0.43 | 0.41 | 0.20 | 0.22 | 0.10 | 0.14 | 0.14 | 0.27 | 0.29 |
| Al | 0.23 | 0.09 | 0.03 | < | < | 0.02 | < | < | < | 0.04 | < | 0.02 | 0.02 |
| In | 0.02 | 0.12 | 0.07 | 0.04 | 0.04 | 0.05 | 0.04 | 0.09 | 0.07 | 0.09 | 0.11 | 0.09 | 0.11 |
| Si | 1.69 | < | < | 3.51 | 3.45 | 3.39 | 6.56 | 7.10 | 7.37 | 7.08 | 6.89 | 4.43 | 4.67 |
| Ag | < | < | < | < | < | < | < | < | < | < | < | < | < |

soft. This is rationalized by the total Ca-Mg concentration being a value of 4.35 ppm. Of the remaining well waters 2A and 7A can be considered as soft waters with total Ca-Mg levels of 3.45 and 8.45 ppm. The other well waters, 3A, 4A and 5A, can be considered hard with Ca-Mg levels of 83, 99 and 94 ppm.

Well waters with the label A designates prior to water treatment and B designates after treatment. Not all of the samples received underwent treatment.

Samples 2 and 5 were water softened. This is readily noticeable as the concentration levels for Ca and Mg decreased. The K, Sr, Mn and Fe levels decreased as well. The Na level increased noticeably. This is due to the addition of sodium phosphates in the water softening treatment.

Samples 2 and 7 are classified as soft water. In both of these samples the well water underwent a sedimentation process to remove solids by gravity. The only noticeable change in concentration was for Fe, where the level dropped from approximately 0.5 ppm down to a level below the detection limit of the instrument. In both cases sodium levels were high but not high enough to pose any health hazards.

Sodium intake levels considered normal in adults is 2000 mg daily. The highest sodium level in these samples is 360 ppm for sample 2. Since adult fluid intake averages 1.5 to 3 liters/day, this drinking water would supply 540-1080 mg total sodium intake. Excessive sodium intake is believed to be a factor in hypertension. Thus people with hypertension

must carefully monitor their intake of sodium.

F. Summary

The well water analysis has been summaried in Table XXXII. In this summary these waters have been broken down and categorized on the basis of their treatment - water softener, sedimentation and no treatment.

With the well waters treated via water softening, one notes that the Ca and Mg levels of the two hard waters, #3 and #5, have dropped substantially. Other elements which appear to be affected similarly include Ba, Fe, K, Mn and Sr. Sodium is the only exception. It increases as expected since a sodium compound is used in the water softening treatment.

Well waters undergoing sedimentation treatment appear to affect only one element - Fe. In this case, the iron levels drops to an undetectable level.

Two well waters, #1 and #4, underwent no treatment. This is on account of the high sulfur levels in these samples which cannot be removed via treatment. In such a case the residents would have to bring in all drinking water. Well #1 had an extremely high S level which is not treatable, but well #4 could be treated if desired.

G. Conclusions

ICP emission spectrometry has been shown here to be an effective, rapid and efficient analytical tool, which can be applied for routine analysis, once the sample is in solution

Table XXXII. Data Summary from Well Water Analysis(µg/ml).

# WATER SOFTENER TREATMENT

| ELEMENT | WELL #3 | | WELL #5 | |
|---|---|---|---|---|
| | A | B | A | B |
| Ca | 68.3 | < | 76.0 | 0.45 |
| Mg | 14.8 | 0.07 | 18.1 | 0.12 |
| Ba | 0.08 | < | 0.16 | < |
| Fe | 3.71 | < | 1.26 | < |
| K | 3.48 | 0.45 | 3.08 | 1.20 |
| Mn | 0.37 | < | 0.33 | < |
| Sr | 0.65 | < | 0.65 | < |
| Na | 64.5 | 188 | 41.1 | 173 |

Table XXXII. Continued.

## SEDIMENTATION

| ELEMENT | WELL #2 A | WELL #2 B | WELL #7 A | WELL #7 B |
|---|---|---|---|---|
| Fe | 0.39 | < | 0.54 | < |

## NO TREATMENT

| ELEMENT | WELL #1 | WELL #4 |
|---|---|---|
| Na | 290 | 20.6 |
| S | 3.35 | 0.65 |

form. This still remains as a stumbling block in spectrochemical methods of analysis. Until this hurdle is simplified, shortened or surpassed, the chemist will still face wet chemical problems along with his spectral problems.

The plasma is close to being an ideal method for multielement analysis of a wide variety of samples. The ICP also has the capability of performing analysis on a small quantity fo sample.

The ICP has been demonstrated to give reliable analytical data for 13 elements (Al, B, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P and Zn) in plant tissue samples and 21 elements (Al, As, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P, Pb, Sb, Si, Sn, Sr, Ti, V, Zn and Zr) in coal samples. Results are well within the anticipated range of variance for these elements.

In most cases a relative precision of better than 5% for major and minor constituents was obtained for the samples analyzed. This precision includes random errors from instrument measurements as well as errors in sample preparation.

A detailed assessment of the accuracy of determination with trace analytical methods needs to be obtained for the ICP. This can only be accomplished when a greater variety of reference materials are made available.

Presently the slowest step in analysis is converting solid samples into solution form. More work must be done in this area. The 'best' method of dissolution must have the following characteristics: safe, time efficient, use of common equipment, low possibility of contamination, low dilution,

easily standardized, nebulizer compatible and good recovery (38).

Once in solution form, automation of sample introduction into the excitation source will enable analyses with greater sample throughput and little operator assistance.

ICP/AES is very popular presently and is expected to expand further into routine analysis laboratories as a wider selection of commerical instrumentation explodes onto the market. The changeover will be slow, but eventually most routine analyses to determine elemental composition will be done with a plasma excitation source.

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# APPENDIX A

Table A.I. Brief Summary of Programs Available on the 34000 ICP.

```
* COMMAND?  ICP

SYMB, DLOG, TASK, INIT, CAL, A, ASET, BSET, DLIST, RPT1,
RPT2, RPT3, SCAN, NORM, REV, AUX, CURVE, CORR, STATS, DL, HELP,

* COMMAND?  HELP

SYMB - DEFINE INSTRUMENT CONFIGURATION.
DLOG - TO RUN 34000 DIAGNOSTICS AND CREATE DAILY
       Q.C. AND INSTRUMENT LOG.
TASK - TO CREATE/EDIT AN ANALYTICAL TASK DEFINITION FILE.
INIT - TO ESTABLISH FIRST NORMALIZATION INTENSITIES FOR A TASK.
CAL  - TO ACQUIRE DATA FROM CALIBRATION STANDARDS AND
       INITIALIZE NORMALIZATION.
CORR - TO DEFINE CORRECTION COEFFICIENTS FOR SPECTRAL EFFECTS.
A    - ROUTINE ANALYSIS.
ASET - TO DETERMINE A LIST OF SAMPLE NAMES WHEN USING
       AUTOSAMPLER FOR ANALYSIS.
BSET - TO DEFINE BACKGROUND MEASUREMENT POSITIONS FOR AN
       ANALYTICAL TASK USING SAMI.
DLIST- TO PRINT OUT A LIST OF SAMPLE NAMES FROM A RESULT
       STORAGE FILE.
RPT1 - TO LIST A COMPLETE RESULT FILE.
RPT2 - TO PRINT OUT A RESULT FILE IN COLUMN FORMAT.
RPT3 - TO SUMMARIZE STATISTICS ON UP TO FOUR REPEAT ANALYSES
       ON ONE SAMPLE USING STORED RESULT DATA.
NORM - TO REMEASURE NORMALIZATION SAMPLES AND UPDATE DRIFT
       CORRECTIONS.
REV  - TO LIST THE RECENT NORMALIZATION HISTORY FOR A TASK.
STATS- TO MAKE REPEAT INTENSITY MEASUREMENTS AND PRINT
       STATISTICAL SUMMARY.
DL   - TO ACQUIRE INTENSITIES AND CALCULATE DETECTION LIMITS.
CURVE- OFFLINE GENERAL PURPOSE POLYNOMIAL REGRESSION ROUTINE.
AUX  - THE EXECUTIVE THAT WILL ACCESS THE DIAGNOSTIC PROGRAMS.
HELP - THAT'S HOW YOU GOT THIS LIST.

SYMBOLS USED --

<CR>      = RETURN = CARRIAGE RETURN KEY.
<CTRL P>  = CTRL + P KEYS AT SAME TIME; TYPE 'RUN' TO RESTART.
<CTRL X>  = CTRL + X KEYS AT SAME TIME; PROGRAM ABORTS TO
            NEXT ROUTINE.
[START]   = START BUTTON ON 34000 SPECTROMETER.
            THIS IS NOT A KEYBOARD COMMAND, BUT AN ALTERNATE
            WAY OF INITIATING THE ANALYSIS CYCLE.

* COMMAND?  AUX

AUX COMMAND ?  HELP

PROGRAMS AVAILABLE IN THE AUXILIARY EXECUTIVE

EXPRO - CONTINUOUS PROFILING OF A GIVEN CHANNEL NUMBER
EXREF - CONTINUOUS MONITORING OF A GIVEN DIAGNOSTIC NUMBER
TSTLP - STATISTICS WITH TEST LAMP ON
DV    - INTENSITY RESULTS OF A SINGLE INTEGRATION
ICP   - RETURN TO ICP EXECUTIVE
HELP  - THAT'S HOW YOU GOT THIS LIST
```

Table A.II. Initial Analytical Setup on the 34000 ICP.

TASK: DEFINE THE ANALYTICAL CONDITIONS FOR THE ANALYSIS ROUTINE.

CAL: RUN CALIBRATION STANDARDS.

A: ANALZES SAMPLES AND PRINTS OUT THE CONCENTRATION LEVELS FOR THE SAMPLES.

RPT1:
RPT2: REPORTS THE RESULTS.
RPT3:

Table A.III. Routine Analytical Sequence on the 34000 ICP.

| | |
|---|---|
| NORM: | UPDATES THE SLOPE AND INTERCEPT FOR THE CALIBRATION STANDARDS. |
| A: | ANALYZES SAMPLES AND PRINTS OUT THE CONCENTRATION LEVELS FOR SAMPLES. |
| RPT1:<br>RPT2:<br>RPT3: | REPORTS THE RESULTS. |